

Polymerization of Ethene and Branched α -olefins with Group IV Metal Complexes Bearing Nitrogen- and Oxygen-Based Ligands

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Academic Dissertation

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Abstract

The commodity plastics that are used in our everyday lives are based on polyolefin resins and they find wide variety of applications in several areas. Most of the production is carried out in catalyzed low pressure processes. As a consequence polymerization of ethene and α -olefins has been one of the focus areas for catalyst research both in industry and academia. Enormous amount of effort have been dedicated to fine tune the processes and to obtain better control of the polymerization and to produce tailored polymer structures

The literature review of the thesis concentrates on the use of Group IV metal complexes as catalysts for polymerization of ethene and branched α -olefins. More precisely the review is focused on the use of complexes bearing [O,O] and [O,N] type ligands which have gained considerable interest. Effects of the ligand framework as well as mechanical and fluxional behaviour of the complexes are discussed.

The experimental part consists mainly of development of new Group IV metal complexes bearing [O,O] and [O,N] ligands and their use as catalysts precursors in ethene polymerization. Part of the experimental work deals with usage of high-throughput techniques in tailoring properties of new polymer materials which are synthesized using Group IV complexes as catalysts.

It is known that the by changing the steric and electronic properties of the ligand framework it is possible to fine tune the catalyst and to gain control over the polymerization reaction. This is why in this thesis the complex structures were designed so that the ligand frameworks could be fairly easily modified. All together 14 complexes were synthesised and used as catalysts in ethene polymerizations. It was found that the ligand framework did have an impact within the studied catalyst families. The activities of the catalysts were affected by the changes in complex structure and also effects on the produced polymers were observed: molecular weights and molecular weight distributions were depended on the used catalyst structure. Some catalysts also produced bi- or multi-modal polymers.

During last decade high-throughput techniques developed in pharmaceutical industries have been adopted into polyolefin research in order to speed-up and optimize the catalyst candidates. These methods can now be regarded as established method suitable for both academia and industry alike. These high-throughput techniques were used in tailoring poly(4-methyl-1-pentene) polymers which were synthesized using Group IV metal complexes as catalysts. This work done in this thesis represents the first successful example where the high-throughput synthesis techniques are combined with high-throughput mechanical testing techniques to speed-up the discovery process for new polymer materials.

Preface

The experimental part of this thesis was carried out between 2004 and 2007 in the laboratory of Inorganic Chemistry. A research period from March 2006 to September 2006 was spent at Symyx Technologies Inc, in Santa Clara, California. Financial support from the Academy of Finland (Projects 209739 and 123248) and from the Science Foundation of University of Helsinki is gratefully acknowledged.

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List of Original Publications:

- I Pärssinen Antti, Elo Pertti, Klinga Martti, Leskelä Markku, Repo Timo: Synthesis of titanium complexes bearing two mono anionic malonic acid ester based ligands and their use as catalyst precursors in ethene polymerization. *Inorganic Chemistry Communications* **2006**, 9(8), 859-861
- II Räisänen Minna T., Elo Pertti, Kettunen, Mika, Klinga Martti, Leskelä Markku, Repo Timo: Practical method for 2-hydroxyphenylketimine synthesis. *Synthetic Communications* **2007**, 37(11), 1765-1777
- III Elo Pertti, Pärssinen Antti, Nieger Martin, Leskelä Markku, Repo Timo: Synthesis, ethylene polymerization and dynamic features of titanium and zirconium complexes bearing chelating malonate based enaminoketonato ligands *Journal of Organometallic Chemistry*, **2009**, 694(18), 2927-2933
- IV Elo Pertti, Pärssinen Antti, Rautiainen Sari, Nieger Martin, Leskelä Markku, Repo Timo: Titanium complexes with modifiable pyrazolonato and pyrazolonato-ketimine ligands: Synthesis, characterization and ethylene polymerization behavior *Journal of Organometallic Chemistry*, *in press*
- V Elo Pertti, Schofer Susan, Hahn Hyeok, Hajduk Damian, Murphy Vince, Diamond Gary, Doolen Robert, Huetten Frank, Chen Ying, Sharma Anushka: Rapid Discovery and Physical Characterization of a Family of Polyolefins Using High Throughput Techniques *Manuscript*

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Abbreviations

| | |
|----------------|-------------------------------------|
| TMA | Trimethyl Aluminium |
| MAO | Methylaluminiumoxane |
| PE | Polyethene |
| HDPE | High Density Polyethene |
| LDPE | Low Density Polyethene |
| LLDPE | Linear Low Density Polyethene |
| PP | Polypropene |
| TIBA | Tri-Isobutylaluminium |
| MMAO | Modified MAO |
| Cp | Cyclopentadienyl |
| 4M1P | 4-methyl-1-pentene |
| P4M1P | Poly(4-methyl-1-pentene) |
| NMR | Nuclear Magnetic Resonance |
| EA | Elemental Analysis |
| MS | Mass Spectrometry |
| <i>n</i> -BuLi | <i>n</i> -Butyllithium |
| GPC | Gel Permeatation Chromatography |
| <i>i</i> Pr | iso-Propyl |
| DMAO | Depleted Methylaluminiumoxane |
| acac | acetylacetonato |
| dbm | dibenzoylmethanate |
| <i>t</i> -Bu | tert-butyl |
| HTS | High-Throughput Screening |
| PPR | Parallel Pressure Reactor |
| DMTA | Dynamic Mechanical Thermal Analysis |

1 Introduction

56 years ago, in 1953, Karl Ziegler made a breakthrough discovery while working with “Aufbaureaktion”. He synthesized high density polyethene (HDPE) using zirconium and titanium halides in the presence of aluminium alkyls under mild conditions.¹ In 1954 Giulio Natta, whose assistant was present while Karl Ziegler made his historical discovery, applied the same concept and was successful in producing, for the first time, crystalline isotactic polypropene.^{2,3} After characterization of the ordered polypropene Natta defined the terms that are still used to describe stereorestructures of polymers: atactic, syndiotactic and isotactic.⁴ In 1963 both Karl Ziegler and Giulio Natta were awarded with the Nobel Prize for their invention.

After the original discovery, Ziegler-Natta catalysts have been developed to achieve higher productivities and better stereoselectivity. The current state-of-the-art Ziegler-Natta catalyst comprises of MgCl_2 support, TiCl_4 , aluminium alkyl(s) and internal- and/or external-donor(s).⁵⁻⁹ Even though the performance of Ziegler-Natta catalysts have been greatly improved, they have an inherent characteristic of being “multisite” catalysts, i.e. the environment around the active sites varies resulting in broad molecular weight distributions as well as variations in stereoselectivity.

Well-defined, homogeneous, “single-site” catalysts provide a solution for this drawback of heterogeneous Ziegler-Natta catalysts. The development of these homogeneous catalysts began via the usage of aluminium alkyl activated titanocene derivatives in ethene polymerization.¹⁰⁻¹³ Unfortunately aluminium alkyl activation did not afford high activities. In 1975 an enormous increase in activity was achieved by using titanocene dichloride complexes in combination with TMA (trimethylaluminium) and a substantial amount of water.¹⁴ The rise in activity was explained by the formation of MAO (methylaluminiumoxane) through hydrolysis of TMA. This was later confirmed with the activation of titanocenes and zirconocenes by using a preformed MAO.^{15,16} Following these discoveries a vast number of patents and academic papers concerning metallocene catalyzed olefin polymerization have been published. Today metallocene catalysts are well-studied and they can be fine-tuned to produce a number of different poly(α -olefin) structures.¹⁷⁻²¹

Following the success of metallocene mediated polymerization, a number of different homogeneous catalysts have been developed. Using these novel catalysts new polymer types, which have not been accessible through Ziegler-Natta and metallocene catalysis, have been obtained.^{22,23} The new non-metallocene catalyst systems have used a

wide range of different organic ligand frameworks.^{24,25} The multitude of different ligand options allows one to modify electronic, geometric and steric characteristics of the active site and through this influence the performance of the catalyst. In addition to Group IV metal complexes notable achievements have also been established among Ni, Pd, Fe and Co complexes with diimine and diimine-pyridine ligands.²⁶⁻²⁸ Late transition metal complexes have opened doors for new types of polyolefins including hyperbranched polyethene and copolymers of ethene and polar monomers.²⁶ The development of new catalysts for olefin polymerization continues to be an active area of research in both academic and industrial research groups.²⁹⁻³⁶

2 The Scope of the Thesis

The work done within this thesis can be divided into two parts. The first and major part of the thesis is devoted to the development of new Group IV metal complexes bearing [O,O] and [O,N] ligands and their use as catalyst precursors in ethene polymerization. In the second part high-throughput techniques are used in tailoring properties of new polymer materials which are synthesized using Group IV complexes as catalysts.

The work done earlier, for example with phenoxy-imine- and diimine complexes, has shown that by changing the ligand structure around the metal center it is possible to tailor the performance of the polymerization catalysts.^{26,37,38} For this reason the major part of the thesis was devoted to synthesis of new Group IV metal complexes with modifiable ligand structures. The train of thought was that the use of modifiable ligands would allow greater freedom to alter the environment of the metal centre and so lead to potentially interesting catalyst families. The malonic acid esters were considered to be good ligand candidates since both non-coordinating ends can be varied fairly easily by using different alcoholates in the synthesis. Titanium complexes bearing these ligand structures were synthesized and used in ethene polymerizations (Publication I). These catalysts were further modified by replacing one of the coordinating oxygen atoms with an imino group (Publication III). Also the pyrazolonato and pyrazolonato-ketimine ligands offer multiple sites that can be modified. Six new titanium catalysts bearing these types of ligand structures were synthesized and used in ethene polymerization experiments (Publication IV). The synthesis of the pyrazolonato-ketimine ligands was not, however, straightforward and an autoclave method was developed to synthesize these compounds (Publication II).

During the last decade high-throughput techniques have been adopted into polyolefin research in order to speed up and optimize the catalyst candidates.^{39,40} These methods have already proven their value, for example in the development of Chain-Shuttling polymerization.⁴¹ High-throughput techniques were used in tailoring poly(4-methyl-1-pentene) polymers which were synthesized using Group IV metal complexes as catalyst precursors (Publication V).

3 Literature review

3.1 Background: Polyethene and Polymers of Branched α -olefins and their Applications

Polymers are a part of our daily lives, so much so that it would be hard to imagine life without them. Today, polymers are used practically in all areas of life: in food packaging, water- and gas pipes, cables and cars and in medical applications like joint and bone replacements.⁴²⁻⁴⁵ Polyolefins represent the largest polymer family of thermoplastics with an approximate production of 115 million tons in 2007.⁴⁵ Polyethene (PE) was the major polyolefin with production of over 70 million tons. PE is an affordable material that is versatile and can be manufactured so that it is suitable for various applications. PE materials are classified based on density, branching and molecular weight. In today's industrial processes high-pressure radical polymerization is used to produce LDPE (Low Density Polyethene). This process, however, does not for example allow control of chain branching or chain length. This is why catalyzed low pressure processes, like the slurry process, are used in the production of LLDPE (Linear Low Density Polyethene) and HDPE.^{36,46}

Polymers of branched higher α -olefins are not as common as PE or PP (polypropene). A number of different monomers have been used, including 5-methyl-1-heptene, 4-methyl-1-pentene, 4-methyl-1-hexene, 4-phenyl-1-butene and 3-methyl-1-pentene. Also more complex monomers, like 3,5,5-Trimethyl-1-hexene have been utilized.^{47,48} The chemical properties of most polymers of branched α -olefins resemble those of PP; they resist most inorganic and organic acids and bases as well as most solvents. However, the branched poly(α -olefins) have two tertiary C-H bonds in each monomer unit and this makes such polymer susceptible to oxidative degradation reactions. The mechanical and physical properties of these polyolefins are depended on the length and nature of the side chain and the structure of the polymers.⁴⁹ Higher production costs hinder commercialization of these products but they have found their

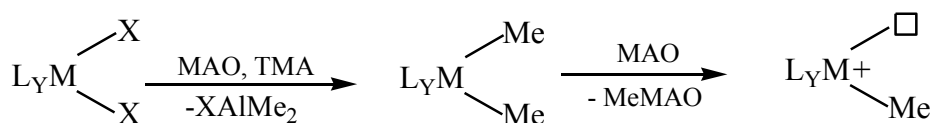
place as speciality polymers. For example poly(4-methyl-1-pentene) (P4M1P) is produced by Mitsui Chemicals under trade name TPX.⁵⁰ P4M1P has found extensive use in medical applications due to its beneficial properties like high transparency, thermal stability and chemical resistance.^{49,50}

3.2 Non-metallocene Group IV Complexes Bearing [O,O] and [O,N] ligands in Ethene Polymerization

As mentioned earlier, a vast number of Group IV non-metallocene complexes with many diverse ligand structures have been published and used as catalysts in ethene polymerizations. This literature review focuses on the development of complexes bearing [O,O] and [O,N] ligands which have gained a considerable interest especially since the mid-1990s. This interest is due to the fact that metallocene catalysts are well patented and these non-metallocene catalysts with single-site properties offer an attractive alternative. Most complexes are in dichloride form and as such need a suitable activator before they can be used as catalysts in a polymerization reaction.⁵¹ MAO is by far the most common activator for Group IV complexes, but also borate and borane activation with reagents like $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{PhNHMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ and $\text{B}(\text{C}_6\text{F}_5)_3$ have been utilized as cocatalysts in combination with appropriate alkylating agents such as TMA and TIBA (tri-isobutylaluminium).⁵²⁻⁵⁵ In addition to the above mentioned activators, modified MAO (MMAO) has lately gained considerable interest as an alternative activator. MMAO, which is prepared by controlled hydrolysis of TMA and TIBA, is more soluble than MAO and has an enhanced storage stability.⁵⁶

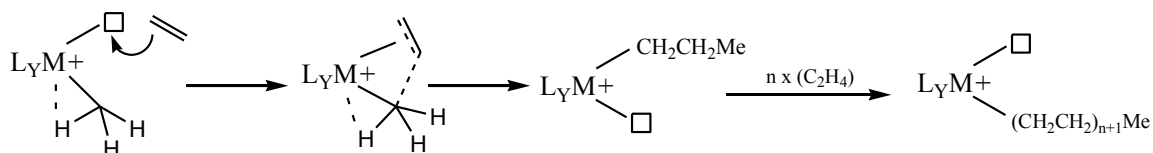
3.2.1 Polymerization Mechanism

As already discussed, MAO is often chosen as the cocatalyst for Group IV metal complexes. As depicted in Scheme 1 MAO has two roles in activation step: firstly it alkylates the metal complex and secondly it abstracts one of the alkyl groups to form an active species.^{15,16} The rate of alkylation and the abstraction process is affected by the nature of the metal, the ligand structure around it and by the chemical nature of the labile leaving groups. According to this mechanism potential ligand structures should be designed so that they do not donate too much electron density to the metal center and consequently diminish the high positive charge of the catalytic site as this can lead to a slower alkylation rate. Halides and alkyl groups are generally preferred as leaving groups.



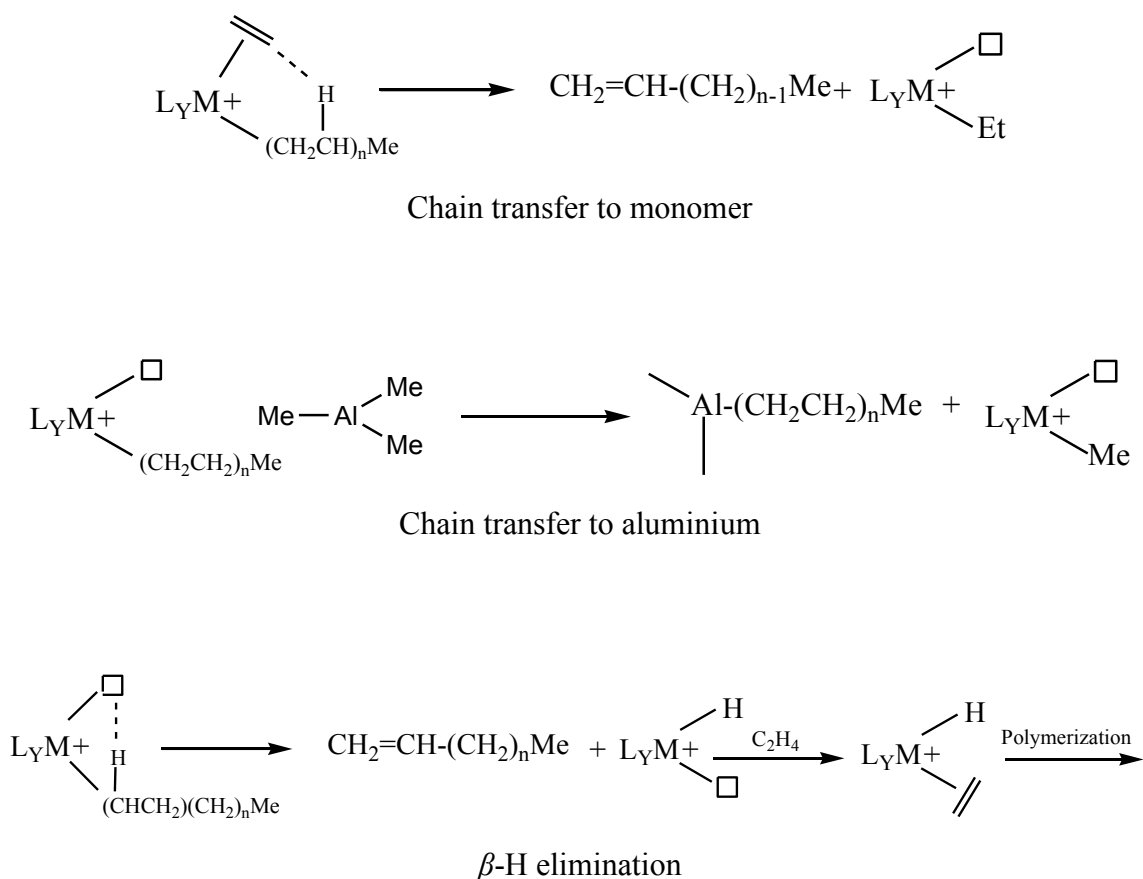
Scheme 1. Activation of Group IV complexes with MAO

The catalytically active sites, which are formed through alkyl abstraction, are strong Lewis acids that can coordinate the olefin monomer to vacant site (Scheme 2). The coordinated monomer is then inserted by migration into the metal-carbon bond to form a longer alkyl-group. Then the chain growth takes place via multiple *cis*-insertions of monomer into the metal-carbon bond. This polymerization mechanism was proposed by Cossee and Arlman and is generally accepted for homogeneous catalysts.⁵⁷ This mechanism requires that the catalyst candidates are designed to have two labile leaving groups in *cis*-positions toward each other to enable fast propagation rates. Complexes bearing leaving groups in *trans*-position towards each other often lead to poor catalysts.⁵⁸ It should be noted, however, that the configuration of complexes are usually determined for dichloride or other non-activated catalysts and it is possible that activated species may adopt a different configuration.



Scheme 2. Propagation step in olefin polymerization

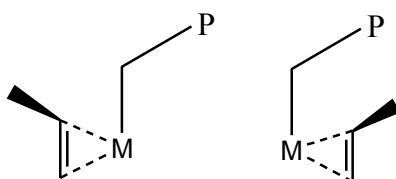
The polymerization reaction is terminated by chain transfer to monomer or to aluminium or by β -H elimination as depicted in Scheme 3. The dominant termination mechanism is depended on the catalyst structure, reaction conditions and the type and amount of used cocatalyst.



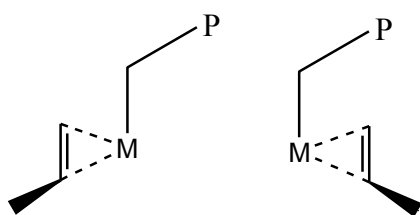
Scheme 3. Termination mechanisms for polymer chain growth.

Propene and other α -olefins can coordinate to the vacant site of the active metal center in four different modes, as depicted in Figure 1. Both primary (1,2) and secondary (2,1) insertions are possible but for α -olefins 1,2-insertions are electronically favoured. It has been shown that the ligand structure around the active metal site determines the position of the growing chain and by doing so also determines the orientation of the coordinating monomer. The single-site catalysts can be designed to give the desired stereoregularity for the polymer product. The isotactic polymers consist of chiral centers of the same configuration whereas syndiotactic polymers comprise of alternative chiral centers. In atactic polymers no order of configuration is present. A schematic representation of the stereoregularity, as it was proposed by Giulio Natta, is depicted in Figure 2.⁴ In addition to the basic structures given in Figure 2, the use of single-site catalysts has also opened doors for synthesis of hemi-isotactic and stereo-block

copolymers.⁵⁹⁻⁶² Moreover, it is also possible to design a dual-side metallocene catalyst to introduce controlled errors to the polypropene chain and so tailor the polymer properties.⁶³



(1,2) propene insertion



(2,1) propene insertion

Figure 1. Possible insertion modes of propene

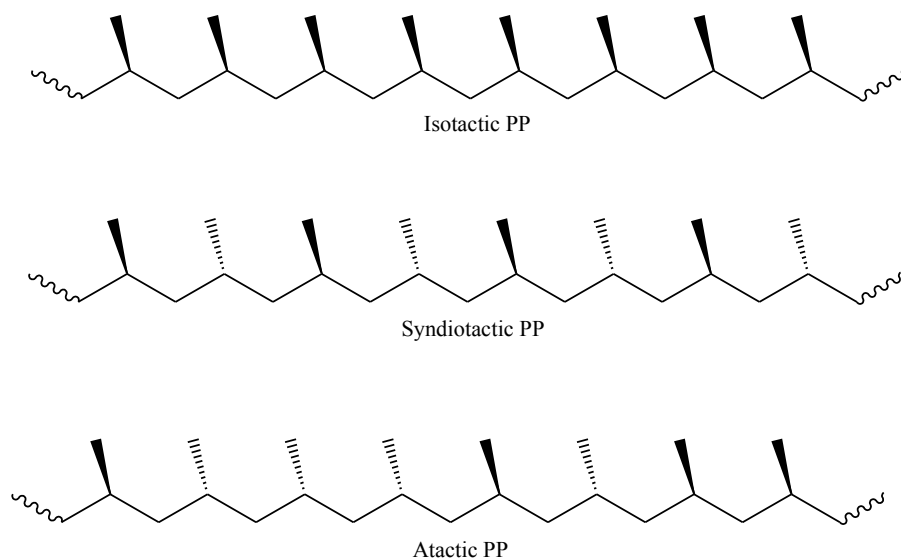


Figure 2. Possible stereostructures for polypropene

3.2.2 Group IV Complexes with [O,O]-type ligands as Catalysts for Ethene Polymerization

Monoanionic alkoxide ligands, are considered to be isonumeral and isolobal with Cp (cyclopentadienyl) ligands, i.e. they can both bind to a metal using one *s* and two *p* orbitals.⁶⁴ In this way alkoxide ligands can donate up to six electrons to the metal center⁶⁵ with two labile halogen or alkyl group this would result in a 16-electron complex and when activated forms a cationic 14-electron species. However, due to the higher electronegativity of oxygen, the alkoxides are more often regarded as four-electron donor ligands.⁶⁶ Applying this concept means that by using [O,O] and [N,O] chelating ligands it is possible to generate cationic 14-electron species.

Complexes with an acetylacetonato (acac) type backbone are known for most transition metals (Figure 3)⁶⁷. Group IV complexes with bis(β -diketonato) ligands have been shown to adopt the *cis*-configuration, which is suitable for α -olefin polymerizations although steric effects can favour the *trans*-isomer.^{68,69} Some of these types of complexes have been utilized as catalysts for ethene polymerization.⁷⁰⁻⁷² Janiak *et al* reported the synthesis of zirconium complexes with acetylacetonate and dibenzoylmethanate (dbm) ligands.⁷⁰ These catalysts were studied by varying the number of chelating ligands and it was found that after MAO activation all the complexes were active in ethene

polymerizations, the maximum activity of $1130 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ was achieved with (dbm)ZrCl₂ complex. The fact that even (acac)₄Zr was active in ethene polymerization implies that the TMA present in MAO is able to remove one or more chelating ligands to generate the active species. All the diketonato-catalysts were able to produce high Mw polyethene with a reasonably narrow molecular weight distribution (PDI close to 3).

The dibenzoylmethane ligand has also been used with a titanium complex.⁷¹ MAO activated (dbm)₂TiCl₂ was found to be less active than the zirconium analogue, exhibiting ethene polymerization activity up to $530 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$. Also, this catalyst system produces polymers with a much broader molecular weight distribution.

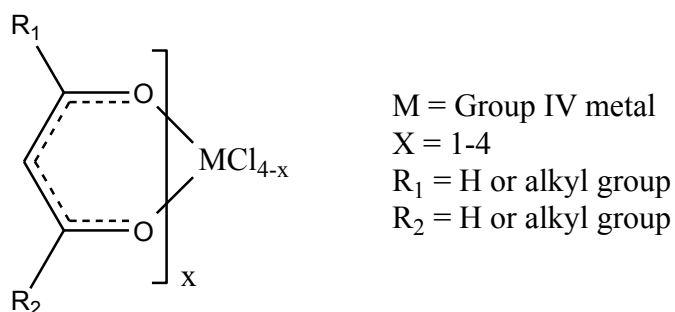


Figure 3. General representation of studied acac-type Group IV metal complexes

The role of the cocatalyst for activation of β -diketonato-complexes was demonstrated by Mitani *et al.*⁷² Zirconium complexes with various acetylacetonato-type ligands were synthesized and activated with different Al-compounds. The use of MAO and TMA as an activator lead to the formation of polyethene while the use of chlorinated aluminium alkyls, like dimethylaluminium chloride, resulted in the formation of oligomeric products. Both the oligomerization activity as well as the distribution of oligomers was dependent on the nature of the substituents in the acetylacetonate backbone.

β -diketonato complexes have also been used as polymerization catalysts for number of other monomers. For example, zirconium acetylacetonato catalysts were able to produce elastic polypropene and the useage of titanium diketonato complexes in the polymerization of styrene resulted in formation of syndiotactic polymer.^{73,74}

A number of complexes bearing one alkoxide group with an additional oxygen donor have been prepared and used in ethene polymerizations.^{54,75-78} Sobota *et al* have investigated such titanium complexes with 3-hydroxy-2-methyl-4-pyrone and 2-

methoxyphenol ligand structures as displayed in Figure 4.⁷⁵ Despite the differences between these ligands only a small effect on catalytic activity was observed. However, in the case of complexes bearing only one ligand the activity difference is more profound favoring the 3-hydroxy-2-methyl-4-pyrone-based catalysts. Also, an effect of the leaving group was observed: the replacement of chloride by an ethoxide group leads to a decreased activity.

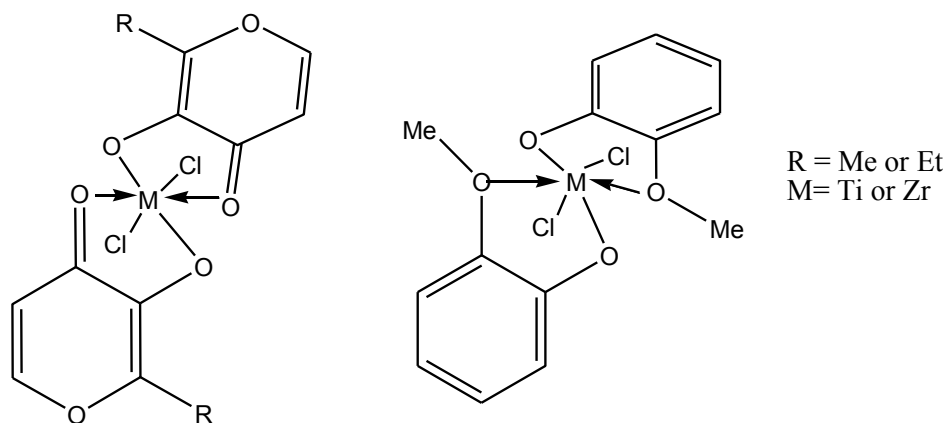


Figure 4. General description of Group IV metal complexes bearing pyrone and methoxyphenol ligands

Basso *et al* have also studied similar catalysts to Sobota.⁷⁶⁻⁷⁸ The zirconium analogue of Sobota's 3-hydroxy-2-methyl-4-pyrone complex proved to be more active than the titanium one. The activity of both the zirconium and titanium catalysts was dependent on polymerization temperature as well as Al/M ratio. However, the zirconium complex was more thermally stable than titanium analogue and the activity was enhanced at higher polymerization temperatures. Also the increase in Al/M ratio led to increased activity. The opposite behaviour was observed for titanium catalysts. It was also noted that unlike the titanium-complex, the zirconium analogue has two stereoisomers when in solution. The MAO activated methyl substituted pyrone-complex was nearly inactive in ethene polymerization. Replacing the methyl group in the pyrone ring with an ethyl one leads to enhanced activity.⁷⁸ According to electrochemical studies the length of the alkyl chain does not affect the electronic density of the metal center. This implies that the improved activity is probably related to better stability of the complex.

Maybe the most notable example of the catalysts with one aryloxy group together with an additional oxygen donor is the one reported by Fujita *et al* (Figure 5).⁵⁴ By changing the carbonyl moiety into an ether one, researchers at Mitsui Chemicals were able to prepare highly active phenoxy-ether catalysts. These catalysts display activities up to 34700 kg mol⁻¹ h⁻¹ with TIBA/ Ph₃CB(C₆F₅)₄ activation. Both the activity of the catalyst and the Mw of the resulting polymer were found to be dependent on the substituent on the *ortho*-position to phenoxy oxygen.

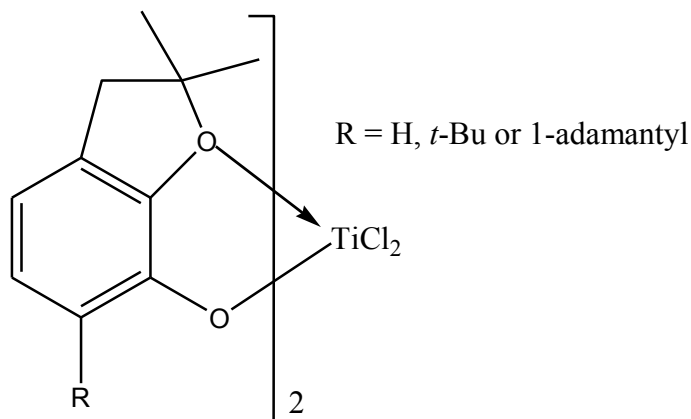


Figure 5. Highly active phenoxy-ether catalyst developed at Mitsui Chemicals

In addition to the above mentioned monoanionic-ligands also number of complexes bearing dianionic [O,O] ligands have been synthesized and tested in ethene polymerizations.⁷⁹⁻⁸¹ Bisphenolato ligands with varying bridges have been shown to be active catalysts for different polymerization reactions. However, it has also been shown, both theoretically and experimentally, that these types of catalysts exhibit better activity when the bridging unit includes additional donor-atom.^{80,81}

Another interesting example of dianionic catalysts is the titanium complex based on the calix[4]arene backbone (Figure 6).⁸² Activation with MAO leads to only moderately active catalyst producing ultrahigh-molecular-weight polyethene. However the catalyst has a good thermal stability and polymerizes ethene at 120°C producing a polymer with narrow (1.3) polydispersity.

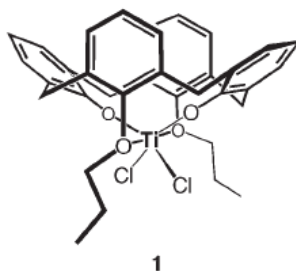


Figure 6. Structure of the thermally stable calyx[4]arene titanium catalyst

3.2.3 Group IV Complexes with [O,N]-type ligands as Catalysts for Ethene Polymerization

[O,N]-type complexes have received considerable interest during the recent years in developing novel highly active polymerization catalysts. Catalyst with salicylaldiminato ligands have especially been in the center of attention (Figure 7). Salicylaldimines were utilized initially by Grubbs and co-workers as ligand precursors for nickel catalysts used in ethene polymerisation.⁸³ Since then the group IV analogues, named FI-catalysts, have been well-studied by many research groups and numerous reports and reviews concerning these complexes have been published.^{36,53,58,84-94} The effects of the metal center and the effects of the substituents in the imino-nitrogen and the *ortho*-phenoxy position have been studied. For the complexes with a *t*-Bu group in the *ortho*-phenoxy position and aniline as the imino moiety, the activity was increased in the order: Zr>Hf>Ti.^{95,96} Increase of the steric bulk in the substituent of the *ortho*-position to the phenoxy leads to improved activity. The complex displayed in Figure 7 with a very bulky cumyl substituent in the *ortho*-position is the most active catalysts known for polymerization of ethene, exhibiting activity up to 6 552 000 kg mol⁻¹ h⁻¹ bar⁻¹.^{36,96} This exceptionally high activity can be explained by two factors: cation-anion separation is enhanced and the bulkier substituent also improves the protection of the phenoxy oxygen which is susceptible to attack by the free TMA present in MAO.

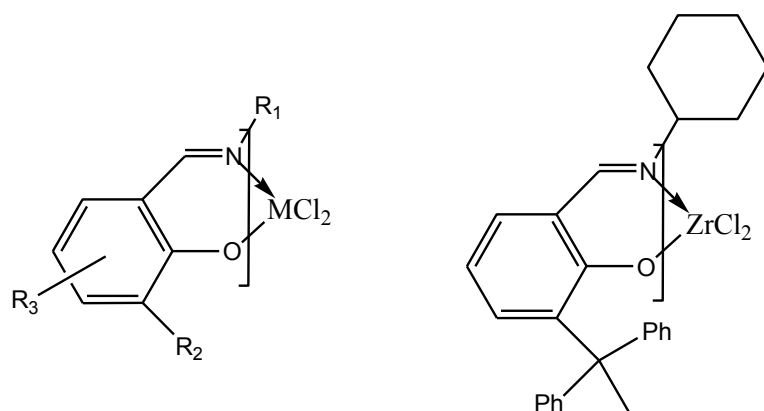


Figure 7. General description of FI-catalysts and schematic structure of the most active ethene polymerization catalyst.

As stated also the variations of imino-substituents have a pronounced effect on the activity of FI-catalysts. Addition of an alkyl substituent in the 2-position of the imino-phenyl lead to significant decrease in activity⁹⁷ and on the other hand the use of fluorine substituent(s) can increase the catalytic activity.⁹⁸ From the studies carried out with alkylphenyl substituents it is evident that not only electronic effects are responsible for gaining good activity; replacing the benzyl-group with an ethylphenyl or propylphenyl one, significantly increases the activity of titanium salicylaldiminato catalysts.⁵⁸ Even more interestingly, these modifications in the imine-group of FI-catalysts can open the door to variations on the resulting polymer structure. FI-catalysts with a fluorinated-phenyl substituent in the imino-position are able to polymerize ethene in a living manner at reasonably high temperatures.^{37,99}

The high performance of the FI-catalysts has prompted many research-groups to study these complexes with diverse conditions and for various applications. FI-catalysts are, for example, able to copolymerize ethene with other monomers to form block-copolymers, are able to produce isotactic and syndiotactic PP with high melting points and offer ways to incorporate polar monomers to PE chains.^{99,101-106}

Bis(phenoxy-ketimine)-catalysts (Figure 8), closely related to the FI-catalysts discussed above, have also been studied in ethene polymerizations.¹⁰⁷⁻¹⁰⁹ Chen *et al* have studied the effect of substituents at the ketimine carbon in ethene polymerizations (Figure 8).¹⁰⁷ The ketimine-catalysts were found to be more active than the aldimine-analogue and the introduction of electron-withdrawing group onto the ketimine carbon atom led to a considerable increase in the activity of these catalysts., an increase in the Mw of the produced PE was also observed. Recently Coates *et al.* have reported the effect of the ketimine substituent on both the activity and selectivity in propene polymerizations.¹⁰⁸

Coates *et al* have also reported the bis(phenoxy-ketimine)-titanium catalyst which interestingly is able to polymerize ethene in a living manner even though the imino-phenyl is not *ortho*-fluorinated.¹⁰⁹ Group IV complexes with bis(phenoxy-ketimine) ligands have also been used as catalysts for example in living polymerization of propene and copolymerization of ethene with polar monomers.^{108,110,111}

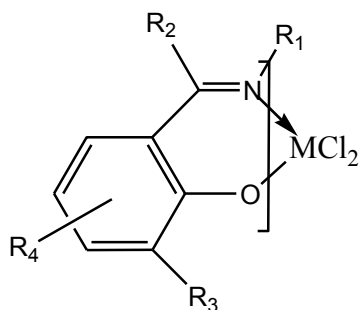


Figure 8. General description of bis(phenoxyketimine) Group IV metal complexes

In addition to ligands based on phenoxides with nitrogen donors, [O,N]-complexes based on an acac-backbone have been studied in ethene polymerizations (Figure 9).¹¹²⁻¹¹⁶ Li *et al* have published several reports describing the use of this type of catalysts in copolymerization of ethene with various other olefins.¹¹¹⁻¹¹⁵ With MMAO activation these types of complexes exhibit high activities and are able to polymerize ethene in a quasi-living manner.¹¹⁴⁻¹¹⁵ The highest activity of 7350 kg mol⁻¹ h⁻¹ bar⁻¹ is obtained with these catalysts when *t*-Bu and CF₃ substituents are used in the acac-backbone and phenyl group with one fluorine in the imino-position.¹¹⁶ However, a decrease in activity was observed if a phenyl group with more fluorine atoms was used. Very recently, closely related imino alkoxide complexes (Figure 9) have been reported, however the stability of these catalysts was extremely poor and as a result also the activity remained low.¹¹⁷

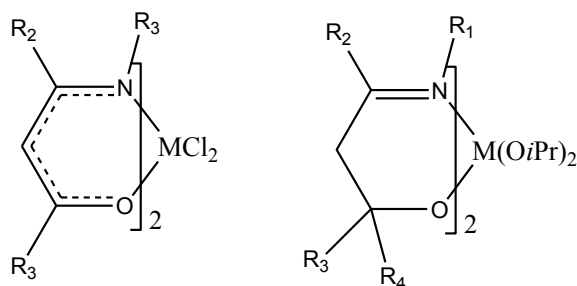


Figure 9. General description of enaminoketonato and imino alkoxide complexes based on acac-type backbone

3.2.4 Fluxional behaviour of group IV metal complexes with [O,O] and [O,N] ligands

As already mentioned [O,O] and [O,N] type complexes may have different isomers when in solution. Generally the complexes can adopt five different configurational isomers as depicted for [O,N]-complexes in Figure 10 and the ratio of different isomers for a given complex can be dependent on both the temperature and the choice of solvent.^{111,76} These isomers may undergo structural changes and several reports describing fluxionality among [O,O and [O,N]-type group IV metal complexes have been published.^{58,116,118,119} The changes in coordination can take place via dissociative mechanisms, however these cases are not common and most rearrangements are attributed to intramolecular processes.¹²⁰ Bailar Twist and Ray-Dutt twists, displayed in Scheme 4, are often used to describe the mechanisms for the intramolecular rearrangements of octahedral complexes.¹²¹

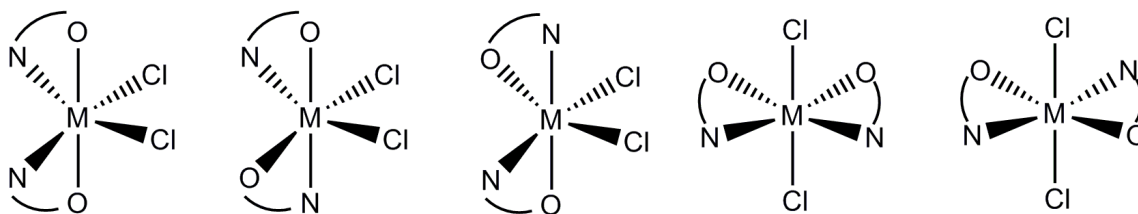
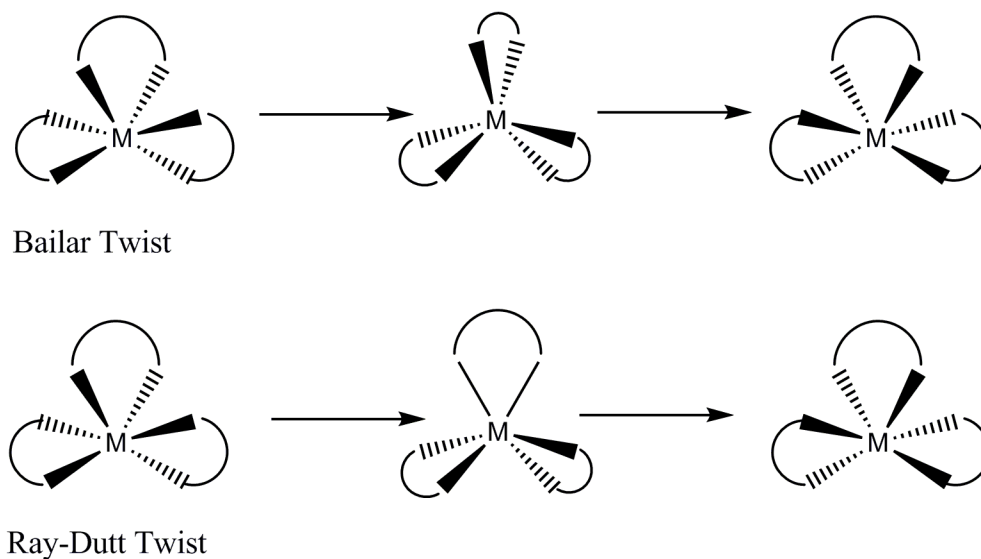


Figure 10. Five different configurational isomers of [O,N]-type complexes



Scheme 4. Bailar and Ray-Dutt twists

Usually it is assumed that activation does not affect the structure of the catalyst and as a result a single well-defined active site is formed.¹²² However, in the reports published quite recently, it has been suggested that the fluxional behaviour of the complex can be the source of the formation of more than one catalytically active site during polymerization experiments.^{118,120,121} Fujita *et al.* have published FI-catalyst capable of polymerizing uni-, bi- and trimodal PE with each molecular weight fraction having narrow MWD value, an indication of single-site character.¹²³ The formation of the different molecular weights was attributed to the fluxional nature of the catalyst precursors. The presence of different isomers and their temperature dependence was later proven by ¹⁵N NMR measurements carried out at different temperatures.¹²³ The activated species of the FI-catalysts have been investigated by NMR using dried MAO (DMAO). Also these experiments supported the formation of more than one active center.^{53,58,119}

Fluxional behaviour of the complex does not always lead to the formation of multimodal PE. In some cases, like the one reported by Li *et al.*, a coalescence of the different isomers can be seen at elevated temperatures¹¹⁶ and as a result the catalysts produced unimodal PE with a narrow MWD. In addition to multimodal PE, for example the formation of PP with an isotactic and atactic blockstructure has been attributed to the fluxional character of the catalyst.¹¹⁸

3.3 Group IV Complexes in Polymerization of Branched α -olefins

Even though polyolefins which consist of branched α -olefins draw less attention than polyethylene or polypropene, they have found a place among speciality polymers. Polymerization of branched α -olefins is more demanding as can be seen from Table 1, which demonstrates the reactivity of these olefins. From Table 1 it can be seen that the reactivities of branched α -olefins in polymerization are lower when compared to propene and that these reactivities are dependent on the size and nature of the branched alkyl group.⁴⁷⁻⁴⁹

Table 1. Reactivities of selected Branched α -olefins

| Olefin | Relative reactivity* |
|--------------------|----------------------|
| Propene | 1 |
| 5-methyl-1-heptene | 0.5 |
| 4-methyl-1-pentene | 0.15 |
| 4-methyl-1-hexene | 0.17 |
| 3-methyl-1-butene | 0.06 |
| 3-methyl-1-pentene | 0.048 |

*Relative reactivities, polymerization experiments carried out under similar conditions with Ti-catalysts

The performance of single-site catalysts has added value over Ziegler-Natta catalysts also in the polymerization of hindered olefins. Single-site catalysts exhibit high stereoselectivity, which is also true in the polymerization of branched α -olefins and this stereoselectivity often exceeds that of conventional Ziegler-Natta catalysts.^{124,125} The high isotacticity, which is achieved through stereocontrol, leads to the formation of polymers with a high melting point. Recently, Miyoshi *et al.* have reported a metallocene catalyzed polymerization of 3-methyl-1-butene which resulted in the formation of polymers with isotacticity over 97%.¹²⁶ Corresponding polymers had melting points up to 304 °C. It is however also clear that the mechanism controlling tacticity of branched polyolefins is not clear and that this mechanism is strongly monomer dependent. For example $\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ catalyzed polymerizations leads to the formation of syndiotactic poly(3-methyl-1-pentene) but, an isotactic polymer is obtained when 4-methyl-1-hexene is used as a monomer.^{127,128}

Even though most reports on the polymerization of branched olefinic monomers with single-site catalysts are based on metallocenes^{124,126-130} and constrained geometry catalysts^{125,131,132}, there have recently been some examples of the usage of non-metallocene complexes in this research area. (Figure 11).^{133,134,139} From these examples it is quite obvious that non-metallocene catalyst can open new doors also in the polymerization of hindered olefins. For instance FI-catalysts were used in the polymerization of 4-methyl-1-pentene and linear α -olefins.¹³³ These catalysts were found to be active and the resulting polymers were highly regio- and stereo irregular. However, the polymers possessed exceptionally high molecular weights, which is quite unique since stereoerrors usually lead to the formation of low molecular weight products¹³⁵⁻¹³⁸. Formation of similar types of polymers were found by Kol *et al.* when chiral salen-type zirconium complexes were used as catalyst precursors.¹³⁹ However, by modifying the ligand backbone the authors were also able to produce isotactic P4M1P.

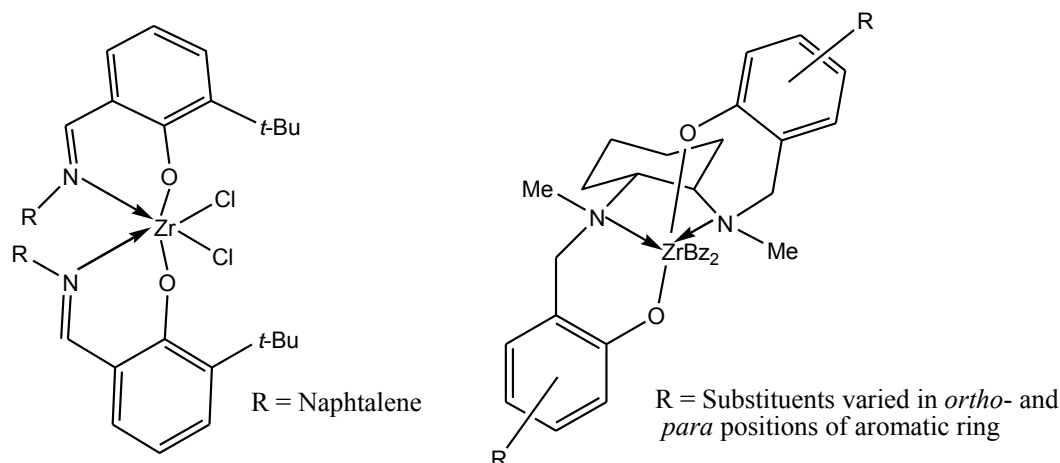


Figure 11. Examples of non-metallocene complexes used as catalysts for polymerization of branched α -olefins.

3.4 High-Throughput Screening Techniques in Development of New Polymerization Catalysts

High-Throughput Screening (HTS) techniques were originally developed for biochemical¹⁴⁰ and pharmaceutical¹⁴¹ applications where the development of new products is both time consuming and expensive. The benefits of these techniques have been obvious and they have been adopted in the development of new polymerization catalysts.^{38,142-145} It is quite clear from the examples in the previous chapters that even minor changes in the complex structure or activation condition can lead to significant changes in the performance of the catalysts or in the properties of the polymer product.^{40,146} Through the use of HTS -techniques new, very promising catalyst families like pyridyl-amide and amino-ether hafnium catalysts have been discovered.^{147,148} The pyridyl-amide catalysts are already used commercially in the production of isotactic polypropene.¹⁴⁹ Another good example of the recent discoveries using HTS-techniques is the chain shuttling polymerization.⁴¹ Arriola *et al* carried out and analyzed more than 1600 polymerization experiments in three weeks. Suitable catalysts and chain shuttling agents were identified to produce ethene based olefin block copolymers with altering semicrystalline and amorphous segments.

It should be understood that the quantity does not prevail over quality: usage of HTS-techniques generates significant amount of data and this data needs to be turned into knowledge. This is why good experimental design is a critical factor in order to reach the desired results, good experimental design will also help the data handling.^{150,151} The issues related to handling data received from HTS experiments have been reviewed by Adams and Schubert.^{152,153} Using HTS-techniques in the development of new polymerization catalysts cannot anymore be considered a new and rising topic; it should be regarded as an established method suitable for both academia and industry alike. Software packages for both information handling as well as instruments for carrying out high-throughput experiments are now commercially available.^{154,155}

4 Results and discussion

4.1 Experimental notes

All the solvents were dried with appropriate drying agents. Reagents of a high purity grade were purchased from commercial sources and used as received. All air sensitive synthesis was carried out either in a glove-box or using standard Schlenk-techniques. ^1H NMR, ^{13}C NMR, EA and EI-MS techniques were used to analyze the obtained synthesis products. Detailed description of the solvent purification, synthesis of ligands and complexes, analyses and polymerization experiments can be found in the experimental part of the attached original publications.

4.2 Malonate Based Group IV Metal Complexes

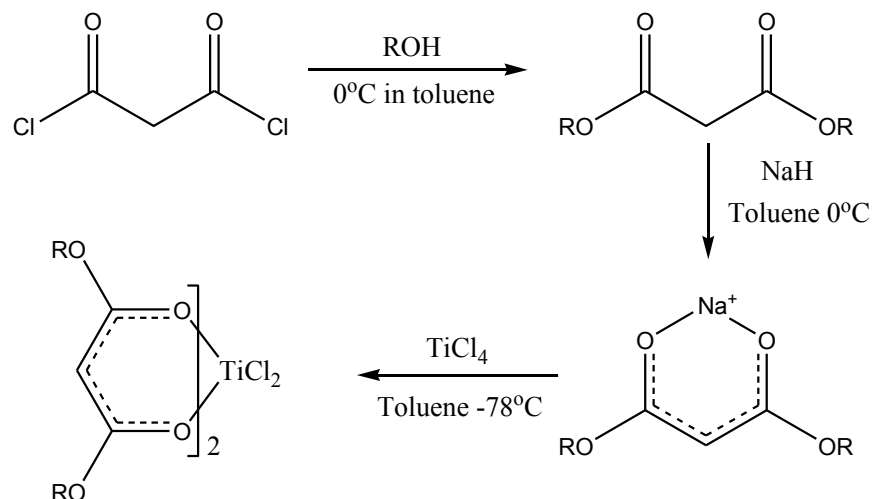
As discussed in the literature review Group IV [O,O]-type complexes have been shown to be active in ethene polymerization^{54,71,82} and complexes bearing acac-type ligands have exhibited activities up to $1130 \text{ kg PE mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$.⁷⁰ A clear influence in the modifications of the ligand framework with these type of catalysts has also been observed. These findings encouraged us to develop catalysts with a easily modifiable malonate-backbone and to test these in ethene polymerization.^I

It has also been shown that Group IV enaminoketonato-complexes based on acac-backbone are effective catalysts for ethene polymerizations.^{115,116} For this reason it was decided to see whether it was possible to improve the performance of malonato-catalysts^I by replacing one of the coordinating oxygen atoms with an imino-group.^{III}

4.2.1 Synthesis and Characterization of Ligands and Complexes

Malonate ligand precursors can be conveniently synthesised by the dropwise addition of a toluene solution of a selected alcohol into the cooled (0°C) solution of malonyl chloride in toluene (Scheme 5). Malonates can also be synthesised by reacting malonic acid with an appropriate alcohol in the presence of POCl_3 .¹⁵⁶ However, it was found that this route leads to unwanted side products and that the purification of the desired product is not always straightforward. Synthesis of corresponding bis(malonato)-titanium complexes was carried out with NaH under mild conditions as displayed in

Scheme 5. Isolated ligand precursors and complexes were characterised by ^1H -NMR- and ^{13}C -NMR spectroscopy and elemental analysis.

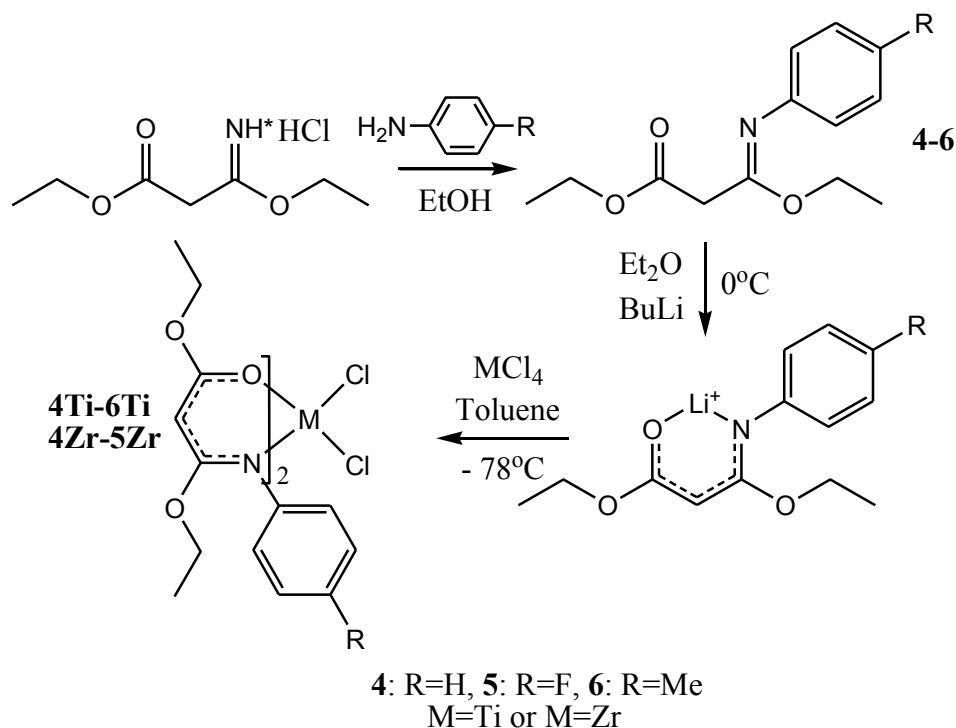


Scheme 5. General route to synthesis of bis(malonato)-titanium complexes.

Eisen *et al.* have also studied bis(malonato)-titanium complexes in olefin polymerization.¹¹⁸ They determined with ^1H -NMR studies that synthesized bis(dimethylmalonato)-bis(diethylamido) titanium complexes have two fluxional processes in solution. The first process is a dynamic one caused by the internal rotation of the diethylamine ligand. The second one arises from the internal rearrangement (Bailar twist) which is seen from the peaks arising from the methoxy groups. In a course of the studies of bis(malonato)-titanium complexes performed within this work no such behaviour was observed. This is most likely due to the fact that the synthesized bis(malonato)-titanium complexes were in dichloride form and so the signals arising from alkoxide-groups are equal.

A general synthetic route for the titanium and zirconium complexes bearing malonate based enaminoketonato ligands is presented in Scheme 6. Ligand precursors were prepared with the chosen anilinium compounds using ethyl 3-ethoxy-3-imino-propionate hydrochloride as a starting material.¹⁵⁷ Ethyl 3-ethoxy-3-imino-propionate hydrochloride was added to an ethanol solution of the chosen anilinium compound.

Zirconium and titanium complexes bearing enaminoketonato ligands were synthesized through lithium salts and pure complexes were obtained by recrystallization from toluene. Isolated ligand precursors and complexes were characterised by ^1H NMR- and ^{13}C -NMR-spectroscopy and elemental analysis.



Scheme 6. General route to synthesis of malonate based bis(enaminoketonato)-titanium and zirconium complexes

Crystals of the complexes **1Ti** and **4Zr** suitable for X-ray structure determination were grown from saturated toluene solutions. The solid-state structures of these complexes are shown in Figures 12 and 13. The X-ray analysis showed that in solid state both complexes adopt distorted octahedral coordination around the metal centre where the two chlorine atoms adopt a *cis*-configuration. In the case of **4Zr** the Zr-N and Zr-O bond lengths resemble those of FI-catalysts reported by Fujita *et al.*⁹⁷ The bond lengths also indicate that in **4Zr** the oxygen is more anionic in nature whereas the bondlength between the nitrogen and zirconium resembles is more closed that expected for coordination type bonding.

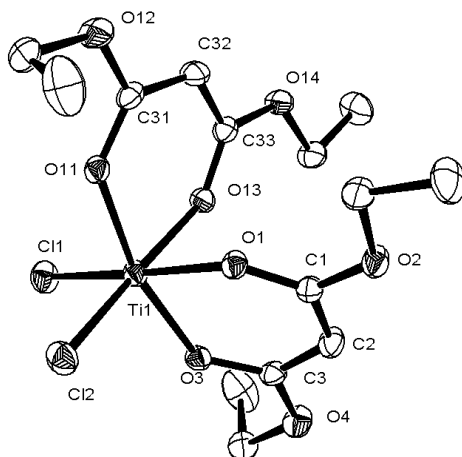


Figure 12. Molecular structure of the complex **1Ti**. Selected bond lengths (Å) and angles (°): Ti–O1 1.944(1), Ti–O2 2.021(2), Ti–Cl1 2.271(1), O1–Ti–O2 83.59(6), O1–Ti–O1 164.95(9), Cl1–Ti–Cl1 96.71(4). Hydrogen atoms are omitted for clarity. ORTEP plot of **1Ti** with thermal ellipsoids drawn at 50% probability level.

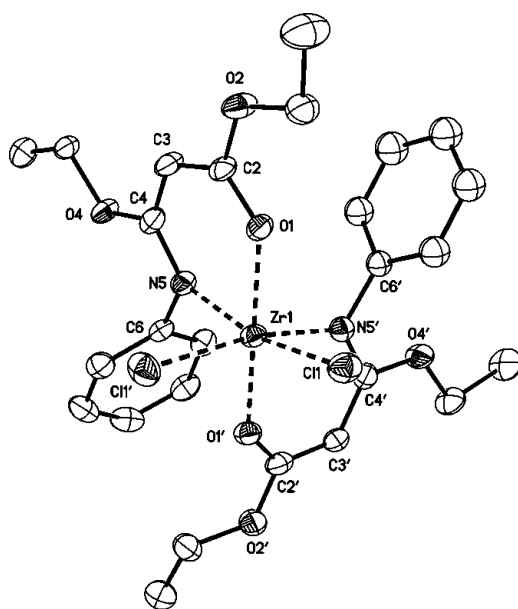


Figure 13. Molecular structure of the complex **4Zr**. Selected bond lengths (Å) and angles (°): Zr–O1 2.069(3), Zr–O1' 2.072(3), Zr–N5 2.235(3), Zr–N5' 2.248(3) Zr–Cl1 2.463(1), N5–Zr1–N5' 90.5(1) O1–Zr–O2 170.6(1), Cl1–Ti–Cl1 93.75(4). Hydrogen atoms and solvent molecules are omitted for clarity. ORTEP plot of **4Zr** with thermal ellipsoids drawn at 50% probability level.

Even though no fluxional behaviour was observed for malonato-complexes, the enaminketonato-complexes **4Ti-6Ti** and **4Zr-5Zr** have two different configurational isomeric structures in solution state. Isomers are clearly seen in ^1H -NMR spectra of **4Zr** displayed in Figures 14-16. These configurational isomers can be identified from the two distinctive singlets in ^1H -NMR spectra attributed to the CH-group in the molecule. Intensity ratios of these singlets are close to 1:2 favouring the isomer having a CH-signal at lower field. The effect of solvent was also observed: when measurements were carried out in less polar d^8 -toluene the ratio of isomers was increased to 1:4 again favouring the isomer having a CH-signal at lower field. No coalescence of chelating protons was observed upon heating, instead the increase in temperature lead to changes in the rotation process of the phenyl ring in one of the isomers. The rotation process was reversible in the studied temperature range. The results from NMR experiments indicate that the solution behaviour of malonate-based enaminketonato complexes is notably different than those previously reported for related complexes, wherein the coalescence of the chelating proton was observed.¹¹⁶ Although the experiments were carried out with dichloride complexes, the presence of two different isomers is a plausible explanation for the polymerization behaviour of these catalysts presented in the following chapter.

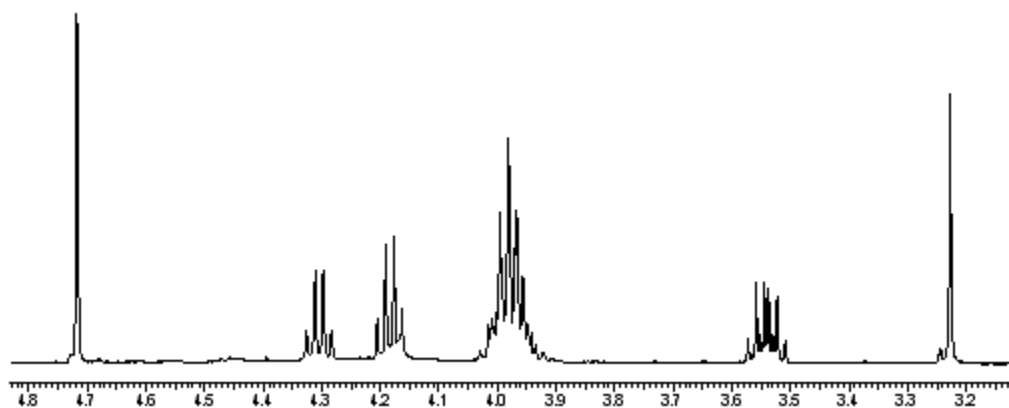


Figure 14. ^1H -NMR spectrum of complex **4Zr** measured in CDCl_3 . Singlets attributed to CH protons in the molecule can be seen at 4.72 and 3.22 ppm. The other signals are attributed to CH_2 protons in the molecule.

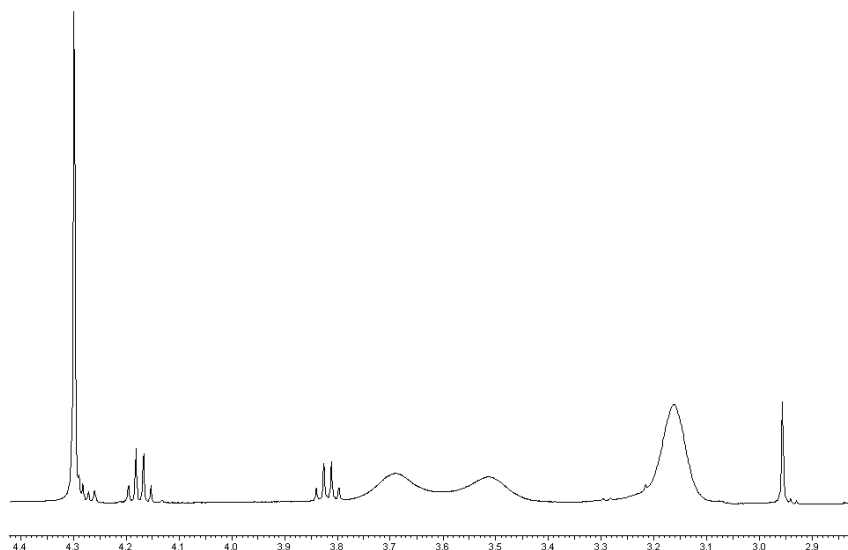


Figure 15. ^1H -NMR spectrum of complex **4Zr** measured in d^8 -toluene. Singlets attributed to CH protons in the molecule can be seen at 4.30 and 2.95 ppm. The other signals are attributed to CH_2 protons in the molecule.

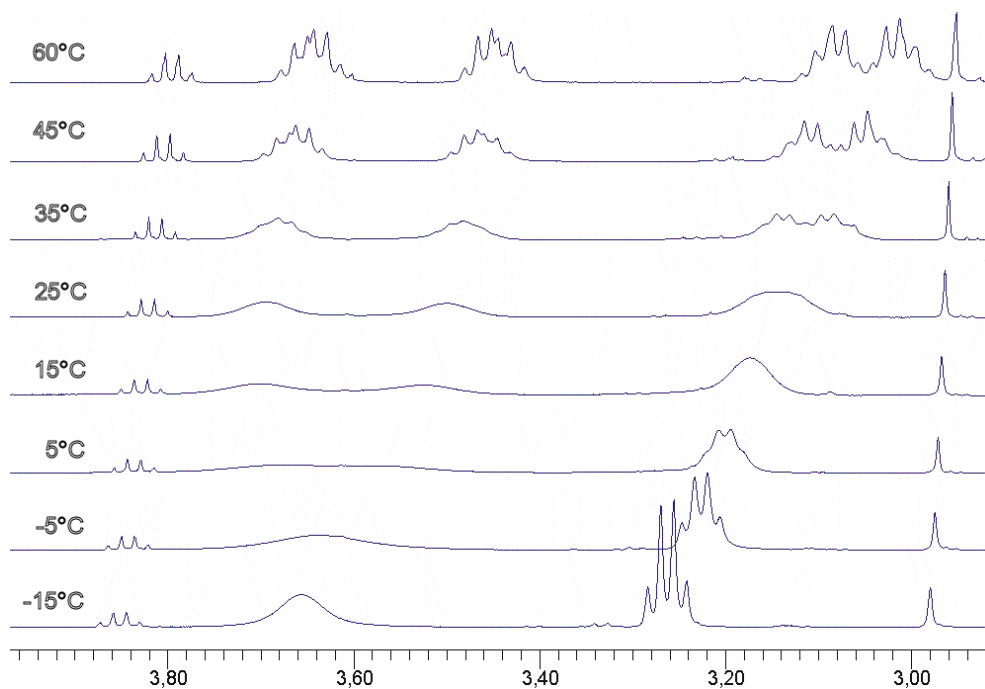


Figure 16. Temperature variable NMR measurements with complex **4Zr** in d^8 -toluene.

4.2.2 Ethene Polymerization Studies

Malonate-complexes were activated with MAO and used as catalyst in ethene polymerizations. The results of these experiments are summarized in Table 2. Bis(malonato)-titanium catalysts exhibited relatively low activities in ethene polymerizations, regardless of the studied ligand framework. Also, no clear effect of the polymerization temperature or monomer pressure on the activity was observed, however a slight decrease in activity with catalysts **1Ti**/MAO was observed when the polymerization temperature was increased. Polymerization temperature had virtually no effect on the activity of **2Ti**/MAO or **3Ti**/MAO.

All bis(malonato) catalysts produced PE with high or ultra high Mw, molecular weights varying between 900 and 3000 kg/mol. The molar mass distributions of all formed PE were rather narrow compared to the related diketonate-catalysts⁷¹ and also an effect of ligand structure on the MWD was observed; in particular catalyst **2Ti**/MAO produced PE with narrow PDI values (varying from 1.3 to 2.2). Polymerization temperature did not have an effect on the MWD of the polymers produced with **2Ti**/MAO, however, the average Mw was clearly decreased with increasing polymerization temperature.

In addition to ethene polymerizations, catalysts **1Ti**/MAO-**3Ti**/MAO were also tested in propene polymerization. Unfortunately no activity was observed. This is in stark contrast to results the obtained with MAO activated bis(dimethylmalonato)-bis(diethylamido) titanium complex which exhibited high activity in propene polymerization (up to 391 kg mol⁻¹ h⁻¹).¹¹⁸ The reasons for these differences are not clear, however propene is known to be much more difficult to purify than ethene and this might be a plausible explanation.

Bis(enaminoketonato) complexes with electron-withdrawing or –donating substituents in the *para*-position of the coordinating imino group were synthesized in order to study how the electronic properties influence the catalytic performance of these catalysts. However, these alternations induced only minor changes in polymerization activities of the catalysts. Still there is an evident effect of the *para*-substituent: the activity increases generally in order *para*-F > *para*-H > *para*-Me. The influence of the *para*-substituents resembles those reported for the related FI-catalyst family.¹⁵⁸ This effect can be explained through enhanced Lewis acidity of the metal center when a more electron withdrawing substituent is used. This in turn, results in an increase in the metal-carbon bond reactivity and reduced activation energy for ethene insertion. The enhanced

Lewis acidity also has an effect on the thermal stability of titanium complexes: a catalyst with *para*-Me substituent is the most thermally stable one and exhibits the highest activity at 60°C. Correspondingly, the catalyst with *para*-F is the least thermally stable and consequently the polymerization activity is decreased when polymerization temperature is increased.

Catalyst **5Ti-7Ti**/MAO and **5Zr-6Zr**/MAO produced PEs with bi- or multimodal MWD. As mentioned before, this feature may be attributed to the dynamic nature of the enaminoketonato-complexes as the molecular weights and the intensities of the low- and high molecular weight part are depended on the polymerization temperature. According to the GPC results these enaminoketonato catalysts produce PEs with relatively broad MWD values indicating non-single-site behaviour. In addition different molecular weight fractions partly overlap with each other leading to even broader molecular weight distribution values. Although in this thesis the NMR experiments were performed on the dichloride complexes, it is reasonable to expect that the fluxional features of the complexes would also be present for the MAO activated catalysts producing bi- and multimodal polyethenes. Similar behaviour has been described for other related [O,N]-type catalysts.^{58,119,123}

The effect of the alkoxy group in the malonate framework on the performance of these catalysts is quite obvious since the related enaminoketonato catalysts based on an acac backbone do not produce multimodal PEs.¹¹⁴⁻¹¹⁶ The role of the alkoxy group is however unclear, the multimodality of the polymers might be caused through fluxionality in the catalytically active species. It is also plausible that the alkoxy groups may have an indirect influence and, for example, enhance the reactions between the catalyst and MAO leading to the formation of multiple active sites.^{58,97,118}

Table 2. Selected ethene polymerization results with MAO-activated complexes 1Ti-6Ti and 4Zr-5Zr/MAO

| Run | Complex | T_p [°C] ^a | p [bar] ^b | Activity ^c | M_w [kg/mol] | M_w/M_n | T_m [°C] |
|-----|---------|-------------------------|----------------------|-----------------------|-----------------|-----------|------------|
| 1 | 1Ti | 60 | 4 | 58 | 1000 | 4,1 | n.d |
| 2 | 1Ti | 40 | 6 | 55 | 900 | 3,8 | n.d |
| 3 | 1Ti | 60 | 6 | 57 | 3000 | 3,2 | n.d |
| 4 | 1Ti | 80 | 6 | 34 | 1600 | 3,9 | n.d |
| 5 | 1Ti | 60 | 8 | 35 | 2500 | 2,5 | n.d |
| 6 | 2Ti | 40 | 6 | 23 | 2900 | 2,1 | n.d |
| 7 | 2Ti | 60 | 6 | 26 | 1300 | 1,9 | n.d |
| 8 | 2Ti | 80 | 6 | 27 | 900 | 2,2 | n.d |
| 9 | 2Ti | 60 | 8 | 21 | 1200 | 1,3 | n.d |
| 10 | 3Ti | 60 | 6 | 19 | 2600 | 3,0 | n.d |
| 11 | 3Ti | 80 | 6 | 14 | 1000 | 2,7 | n.d |
| 12 | 4Ti | 22 | 5 | 27 | 66 / 900 | 6,2 | 135 |
| 13 | 4Ti | 30 | 5 | 66 | 40 / 700 | 8,4 | 136 |
| 14 | 4Ti | 45 | 5 | 31 | 36 / 1200 | Broad* | 135 |
| 15 | 4Ti | 60 | 5 | 26 | 34 / 400 | 15,1 | 138 |
| 16 | 5Ti | 22 | 5 | 85 | 36 / 2400 | Broad* | 135 |
| 17 | 5Ti | 30 | 5 | 59 | 33 / 2300 | Broad* | 137 |
| 18 | 5Ti | 45 | 5 | 36 | 83 / 800 | Broad* | 137 |
| 19 | 5Ti | 60 | 5 | 18 | 42 / 1000 | Broad* | 138 |
| 20 | 6Ti | 22 | 5 | 34 | 3100 | 11,9 | 139 |
| 21 | 6Ti | 30 | 5 | 22 | 63 / 1300 | 13,7 | 136 |
| 22 | 6Ti | 45 | 5 | 29 | 71 / 1300 | Broad* | 135 |
| 23 | 6Ti | 60 | 5 | 50 | 71 / 1000 | 7,3 | 135 |
| 24 | 4Zr | 22 | 5 | 8 | 1.9 / 63 / 1900 | Broad* | 136 |
| 25 | 4Zr | 30 | 5 | 25 | 2.5 / 59 / 1300 | Broad* | 138 |
| 26 | 4Zr | 45 | 5 | 29 | 2.4 / 41 / 1300 | Broad* | 139 |
| 27 | 4Zr | 60 | 5 | 45 | 51 / 1200 | Broad* | 138 |
| 28 | 5Zr | 22 | 5 | 30 | 60 / 1000 | 12,2 | 135 |
| 29 | 5Zr | 30 | 5 | 34 | 71 / 800 | 6,0 | 135 |
| 30 | 5Zr | 45 | 5 | 51 | 78 / 700 | 16,9 | 136 |
| 31 | 5Zr | 60 | 5 | 104 | 76 / 700 | 9,2 | 136 |

[a] Polymerization temperature. [b] Monomer pressure. [c] Activity in (kg PE) / (mol·M·h·bar).

Polymerization conditions: 10 μ mol of catalyst for 1Ti-3Ti and 20 μ mol for others, [Al]/[M] = 2000, polymerization time 30 min.

* Average M_w/M_n value over 20

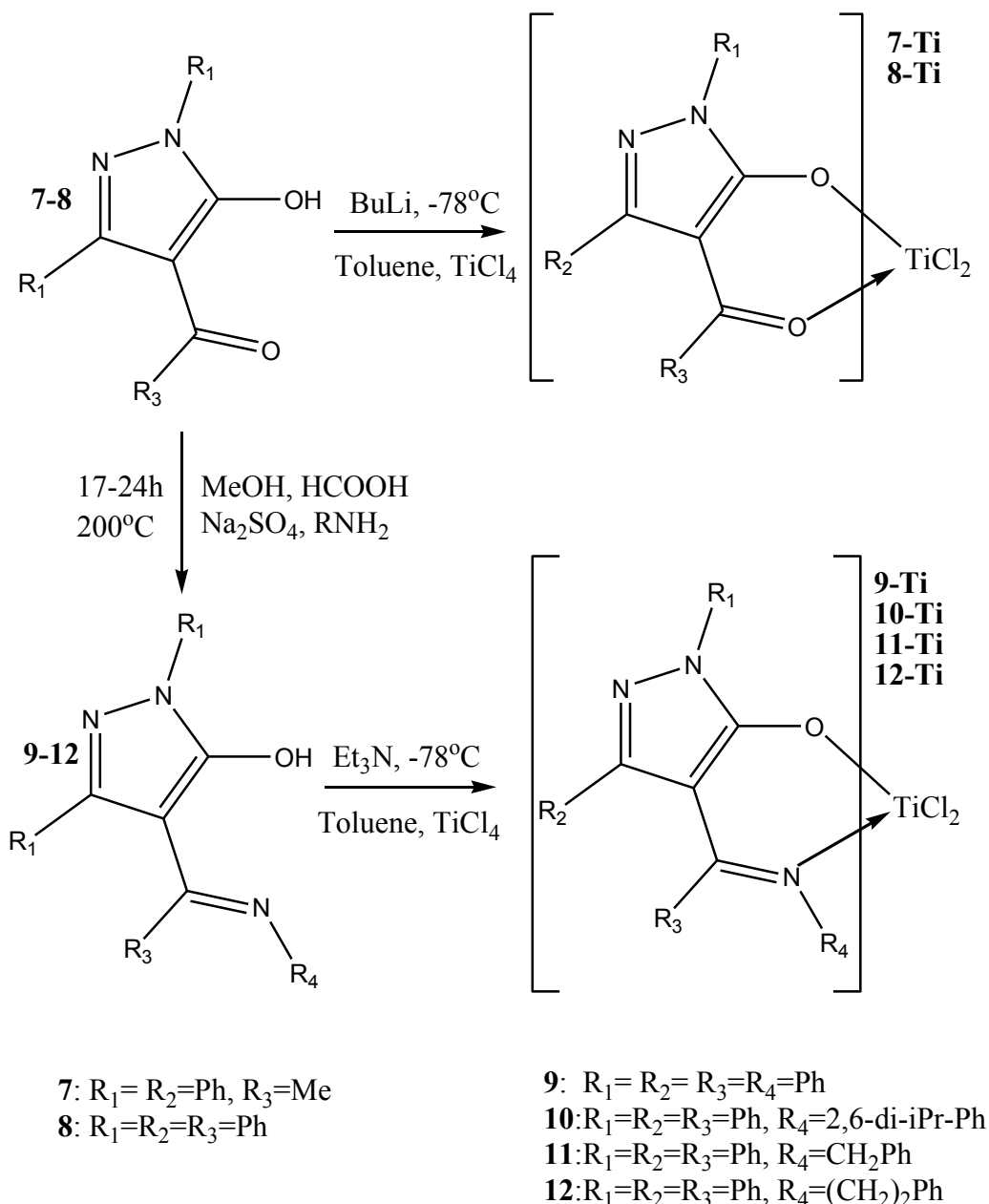
4.3 Pyrazolonato Based Group IV Metal Complexes

Ketimine complexes have attracted less attention than their aldimine analogues. This can be clearly seen when comparing the number of publications describing FI-catalysts and phenoxy-ketimine catalysts. In some cases the ketimines have exhibited higher activities than the aldimine analogues.¹⁰⁷ The lack of interest given to phenoxy-ketimine catalysts may arise from the fact that the synthesis of these complexes is not always straightforward.^{159,160} However, the ketimines have certain benefits, one of them being the possibility of change substituents in the ketimine carbon and in this way influence the performance of the catalyst.¹⁰⁷⁻¹⁰⁹

Within this thesis six titanium complexes bearing pyrazolonato- and pyrazolonato-ketimine ligands were prepared and tested in ethene polymerization. The pyrazolonato-backbone was considered to be an attractive alternative since it offers multiple positions that can be altered. For the work done here, the substituents for the imino-group in the ketimine complexes were chosen in order to compare the ketimine catalysts to the FI-catalysts recently studied in our laboratory.⁵⁸

4.3.1 Synthesis and Characterization of Ligands and Complexes

A general synthetic route for the titanium complexes is presented in Scheme 7. Pyrazolonato ligand precursors **7-8** and corresponding β -diketonato complexes **7Ti** and **8Ti** were prepared according to known literature procedures.^{161,162} The synthesis of pyrazolonato ketimines was not possible through standard imine-synthesis since the condensation reaction between sterically hindered amines and carbonyl compounds is too slow. The reaction is even slower if electron donating substituents, like hydroxy groups, are present. This phenomenon has been observed in the synthesis of other similar compounds.^{159,160} To be able to introduce imine function into the ligand framework, the desired pyrazolonato-ketimine compounds **9-12** were synthesized using an autoclave method^{IV}.



Scheme 7. General synthesis route to of pyrazolonato- and pyrazolonate-ketimine complexes

NMR studies of the pyrazolonato-ketimine compounds revealed that in solution these ligand precursors adopt enol-form. This is clearly indicated by the presence of OH-singlet at low field. Crystals suitable for X-ray analysis for the compounds **9** and **11** were grown from saturated toluene solutions. The structures are displayed in Figures 17 and 18 and selected bond lengths in Table 3. The X-ray analysis revealed that in solid state the pyrazolone-ketimines have a betaine configuration, as can be seen by comparing the bond

distances. The bond between C1-O1 resembles anionic¹⁶³ and the bond between C6-N7 is slightly shorter than that expected for amino configuration but still evidently longer than expected for imino-type compounds¹⁶³ In addition the X-ray structure shows a strong hydrogen bonding¹⁶⁴ between H(N) and O1 forming a six-member ring. Interestingly the aryl-ring attached to the N2 atom is in the same plane as the pyrazolone ring, while the other phenyl rings are out of plane. This indicates that this aryl-ring attached to N2 atom belongs to the same planar conjugated system formed by the betaine moiety.

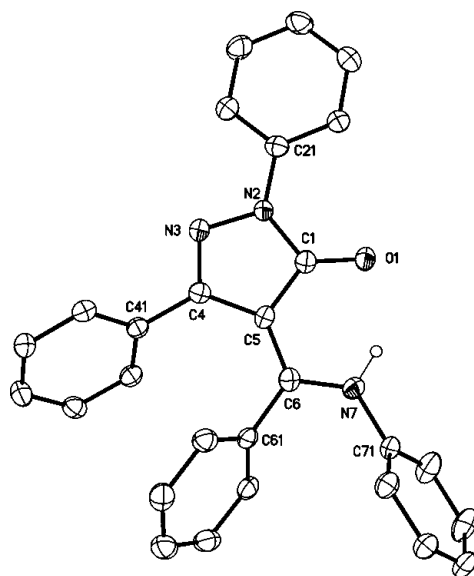


Figure 17. Molecular structure of the ligand **9**. Displacement parameters are drawn at 50% probability level. Hydrogen atoms (except H(N)) are omitted for clarity.

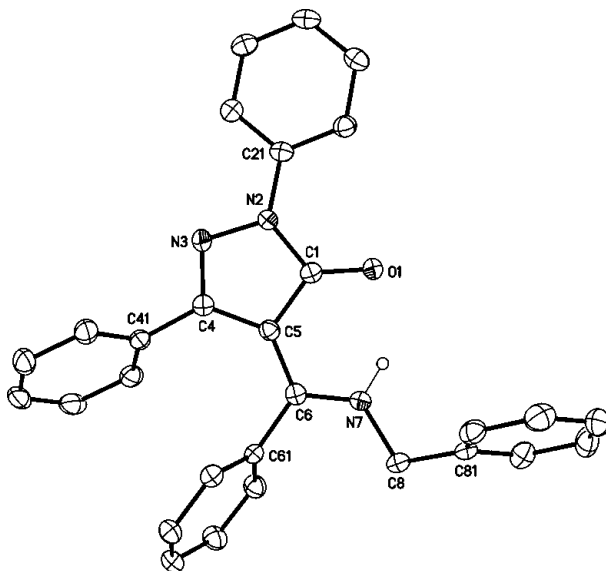


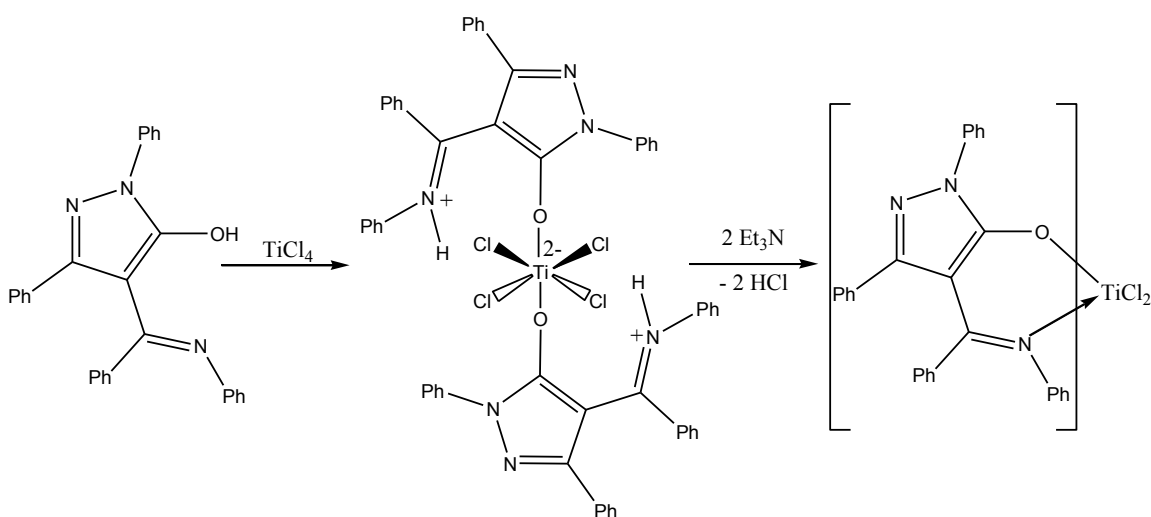
Figure 18. Molecular structure of the ligand **11**. Displacement parameters are drawn at 50% probability level. Hydrogen atoms (except H(N)) are omitted for clarity.

Table 3. Selected bond lengths [Å] for compounds **9**, **11** and **9-Ti***

| Pre-ligand 9 | | Complex 9-Ti* | |
|---------------------|------------|----------------------|------------|
| O1-C1 | 1.247(5) | O1-C1 | 1.283(5) |
| C1-C5 | 1.441(6) | C1-C5 | 1.429(6) |
| C5-C6 | 1.395(6) | C5-C6 | 1.419(7) |
| C6-N7 | 1.344(6) | C6-N7 | 1.327(6) |
| N7-H7 | 0.94(5) | N7-H7 | 0.871(19) |
| Pre-ligand 5 | | Ti1-Cl1 | 2.3604(12) |
| O1-C1 | 1.2492(15) | Ti1-Cl2 | 2.3184(12) |
| C1-C5 | 1.4410(18) | Ti1-O1 | 1.941(3) |
| C5-C6 | 1.4034(18) | O1-Ti1-O1A | 180,00 |
| C6-N7 | 1.3207(17) | O1-Ti1-Cl2 | 88.53(10) |
| N7-C8 | 1.4648(17) | O1A-Ti1-Cl2 | 91.47(10) |
| N7-H7 | 0.884(12) | Cl1-Ti1-Cl1A | 180,00 |

Standard methods of using BuLi or NaH, used for bis(pyrazolonato)-complexes, proved not to be efficient in the synthesis of pyrazolone-ketimine titanium complexes **9Ti** – **12Ti**. The syntheses of Me₃Si-derivates as well as Li- and Na-salts of the compounds **9** and **11** were successful, indicating that the reason for the failed synthesis of titanium complexes was the transmetallation step. However the complexes **9Ti** – **12Ti** were successfully synthesized by first mixing Et₃N with a selected ligand precursor and then adding the resulting mixture to a toluene solution of TiCl₄. Isolated ligand precursors and complexes were characterised by ¹H-NMR-, ¹³C-NMR- and EI-MS-spectroscopy and elemental analysis.

In spite of numerous attempts, no crystals suitable for X-ray crystal structure analysis were obtained for complexes **7-12Ti**. However, the structure of a compound that can be attributed to a reaction intermediate (Scheme 8) was obtained from a toluene solution and is displayed in Figure 19. The obtained structure is a titanium centred trigonal bipyramid coordinated complex with oxygen atoms in axial position to the metal atom. The X-ray analysis also revealed that the reaction intermediate has a crystallographic *Ci*-symmetry. The bond distances between titanium and oxygen resemble anionic and as such are shorter than for example then the ones reported for TiCl₄·2THF or related compounds.¹⁶⁵ The strong hydrogen bond between N(H) and oxygen atom found in the ligand precursor is preserved but weakened. However, two new hydrogen bonds, one weak and one strong, between N(H) and the Cl-atoms Cl1 and Cl2 are formed.¹⁶⁴ The obtained structure for the reaction intermediate correlates well with the one obtained for related salicylaldiminato titanium complex prepared through similar synthesis route.¹⁶⁶



Scheme 8. Formation of intermediate in the synthesis of complex **9Ti**.

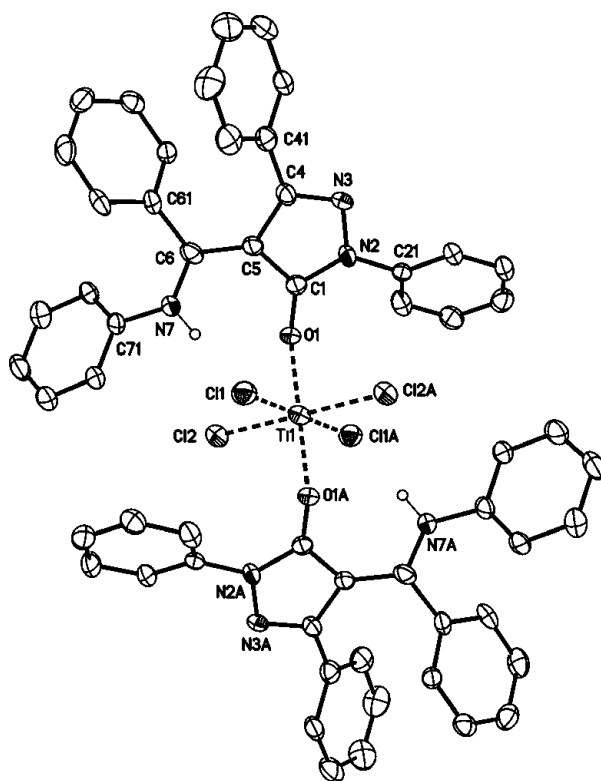


Figure 19. Molecular structure of the reaction intermediate **9-Ti***. Displacement parameters are drawn at 50% probability level. Hydrogen atoms (except H(N)) are omitted for clarity.

4.3.2 Ethene Polymerization Studies

Catalysts **7Ti**/MAO and **8Ti**/MAO with [O,O]-ligands produced unimodal PE as a product, although with a broad MWD. The thermal stability of both catalysts was poor and as a result increased polymerization temperature led to a decrease in activity. An increase in polymerization temperature also led to broader molecular weight distributions. This can be considered as an indication that the catalysts are not stable at higher temperatures and that the increase in temperature might lead to partial decomposition of the complexes. Both diketonato-complexes produced PEs with high or ultra high molecular weight, in general catalyst **7Ti**/MAO produced PE with higher Mw than catalyst **8Ti**/MAO.

Catalyst **9Ti**/MAO with an unsubstituted phenyl group in the imine-part of the complex revealed the highest activities within the pyrazolone-ketimine catalyst family. The highest activity, $612 \text{ kg PE mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$, was observed when polymerization was performed at 60°C . An Increase in polymerization temperature lead to a slight decrease in activity. Catalyst **9Ti**/MAO was also the only catalyst in the family to behave as a single-site catalyst producing PE with a narrow MWD. An effect of polymerization temperature was also observed: at elevated temperature polymers with broader MWD were obtained. With this catalyst there was also a clear effect of monomer pressure on activity: when pressure was increased from 2 to 4 bars the activity was increased from 229 to $612 \text{ kg PE mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$, a further increase in pressure did not anymore lead to greater activity.

Isopropyl (*i*Pr) groups were introduced to 2 and 6 positions of the imino-phenyl ring to see if the performance of the **9Ti**/MAO could be improved by increasing the steric bulk around the metal center. Unfortunately, the enhancement in activity that has been reported for later transition metal catalysts^{167,168} was not observed with the pyrazolone-ketimine catalysts. Instead the activity was drastically decreased. The decrease in activity with increasing steric bulk has also been observed with other Group IV metal complexes.⁹⁷ Changes in monomer pressure or in polymerization temperature did not have a significant effect on the performance of the catalyst or to the structure of the polymer product.

The catalyst precursors were further modified by replacing the aromatic group with a benzyl and ethylphenyl moiety. FI-catalysts with corresponding imino-groups displayed interesting properties in ethene polymerizations⁵⁸ and as mentioned these substituents were selected to have a comparison between these catalyst families. The polymer obtained with catalyst **11Ti**/MAO was clearly a bimodal polymer and the intensities of molecular weight fractions were found to be dependent on the polymerization temperature. With increasing temperature the higher molecular weight fraction became more dominant and correspondingly the intensity of the lower molecular weight fraction was decreased. The polymerization temperature also had a marked effect on the activity of the catalyst, the maximum activity being observed at 60°C followed by a decrease at higher temperatures. No clear effect of monomer pressure was observed.

Formation of a bimodal polymer was observed also when the benzyl group was replaced with an ethylphenyl one. Just like the catalyst **11Ti**/MAO, catalyst **12Ti**/MAO produced PE with the ratios of low- and high molecular weight parts depending on the used polymerization temperature. Similarly the higher molecular weight fraction was dominant when the polymerization was performed at higher temperature. However, in the

case of **12Ti**/MAO the monomer pressure had also an effect, an increase in pressure led to increase in the intensity of the higher molecular weight part. In general, the benzyl substituted catalyst **11Ti**/MAO produced polymers with a higher Mw then the ethylephenyl analogue **12Ti**/MAO.

The polymerization behaviour of **11Ti**/MAO mimics the one reported for the related FI-catalysts.⁵⁸ The low activity of the analogous FI-catalyst was explained by the benzyl substituent partially blocking the active polymerization site. The formation of bimodal PEs was also attributed to this phenomenon. However, interestingly **12Ti**/MAO does not share the similar behaviour to its FI-analogue which exhibited high activity in ethene polymerization and produced monomodal PE with narrow MWD. The reason for the polymerization behaviour of these alkyl-substituted pyrazolonato-ketimine catalysts is not clear.

The reasonably good results obtained with **9Ti**/MAO suggest that the pyrazolone-ketimine catalysts have potential for further development. The complex structure offers many sites which can be modified. Changes in the ketimine-carbon (R_3) would most probably affect the catalytic behaviour of the complexes as well as the substituents in the pyrazolone-ring (R_1 and R_2). In addition fluorinated imino-groups, which have shown interesting properties for FI-catalysts,³⁷ might be interesting for pyrazolonato-catalysts as well.

Table 4. Selected ethene polymerization results with MAO activated complexes **7Ti -12Ti**

| Run | Complex | p [bar] ^a | T _p [°C] ^c | M _w [kg/mol] | M _w /M _n | Activity ^c | T _m [°C] ^d |
|-----|--------------|----------------------|----------------------------------|-------------------------|--------------------------------|-----------------------|----------------------------------|
| 1 | 7-Ti | 4 | 40 | 1020 | 3,1 | 17 | 135 |
| 2 | 7-Ti | 4 | 60 | 960 | 4,7 | 18 | 135 |
| 3 | 7-Ti | 4 | 80 | 980 | 6,6 | 2 | 136 |
| 4 | 7-Ti | 2 | 60 | 820 | 4,7 | 5 | 137 |
| 5 | 7-Ti | 6 | 60 | 1080 | 4,9 | 11 | 135 |
| 6 | 8-Ti | 4 | 40 | 600 | 3,8 | 2 | 135 |
| 7 | 8-Ti | 4 | 60 | 620 | 5,2 | 18 | 135 |
| 8 | 8-Ti | 4 | 80 | 890 | 4,8 | 2 | 136 |
| 9 | 8-Ti | 2 | 60 | 950 | 4,1 | 5 | 135 |
| 10 | 8-Ti | 6 | 60 | 760 | 5,3 | 12 | 137 |
| 11 | 9-Ti | 4 | 40 | 1620 | 1,6 | 342 | 136 |
| 12 | 9-Ti | 4 | 60 | 1020 | 1,6 | 612 | 138 |
| 13 | 9-Ti | 4 | 80 | 690 | 2,2 | 564 | 137 |
| 14 | 9-Ti | 2 | 60 | 1050 | 1,9 | 229 | 138 |
| 15 | 9-Ti | 6 | 60 | 1450 | 1,9 | 590 | 137 |
| 16 | 10-Ti | 4 | 40 | 650 | 7,1 | 22 | 135 |
| 17 | 10-Ti | 4 | 60 | 630 | 7,9 | 25 | 138 |
| 18 | 10-Ti | 4 | 80 | 600 | 3,5 | 35 | 137 |
| 19 | 10-Ti | 2 | 60 | 670 | 5,2 | 24 | 137 |
| 20 | 10-Ti | 6 | 60 | 610 | 4,6 | 32 | 137 |
| 21 | 11-Ti | 4 | 40 | 1410 / 60 | Broad* | 7 | 136 |
| 22 | 11-Ti | 4 | 60 | 1200 / 50 | Broad* | 26 | 137 |
| 23 | 11-Ti | 4 | 80 | 1150 / 50 | Broad* | 5 | 137 |
| 24 | 11-Ti | 2 | 60 | 1170 / 50 | Broad* | 37 | 136 |
| 25 | 11-Ti | 6 | 60 | 1030 / 50 | Broad* | 4 | 137 |
| 26 | 12-Ti | 4 | 40 | 490 / 10 | Broad* | 8 | 135 |
| 27 | 12-Ti | 4 | 60 | 470 / 11 | Broad* | 8 | 135 |
| 28 | 12-Ti | 4 | 80 | 440 / 9 | Broad* | 3 | 136 |
| 29 | 12-Ti | 2 | 60 | 490 / 10 | Broad* | 5 | 136 |
| 30 | 12-Ti | 6 | 60 | 480 / 8 | Broad* | 8 | 135 |

^aMonomer pressure, ^bPolymerization temperature, ^cActivity in kg PE / (molTi·h·bar)^dOnset melting temperature of polyethylene

Polymerization conditions:

Al/Ti = 2000, catalyst amount 20μmol, polymerization time 30 minutes

*Bimodal polymer

4.4 Complexes Bearing Bridged Biphenyl Phenol, Pyridyl- and Heterocyclic-amine Ligands in Homo- and Copolymerization of 4-methyl-1-pentene

As already mentioned in the literature review, P4M1P is used in number of applications including films, packaging and medical and electrical applications.⁴⁹ These applications that are mostly based on the polymers excellent optical transparency, good dielectric properties, high thermal stability, high chemical resistance and high transport properties of light.^{49,50} Only a few articles describing single-site catalyst in the polymerization of 4M1P have been published¹²⁴⁻¹³² and even fewer describe utilization of non-metallocene catalyst.^{133,134,139}

Within this thesis, complexes known to be active and selective in propene polymerizations^{147,169} were chosen as catalyst candidates for polymerization of 4M1P. Basic structures for the used bridged biphenyl-phenol, heterocyclic amine and pyridyl amine complexes are presented in Figure 19. These complexes were activated and utilized as catalysts in this work.

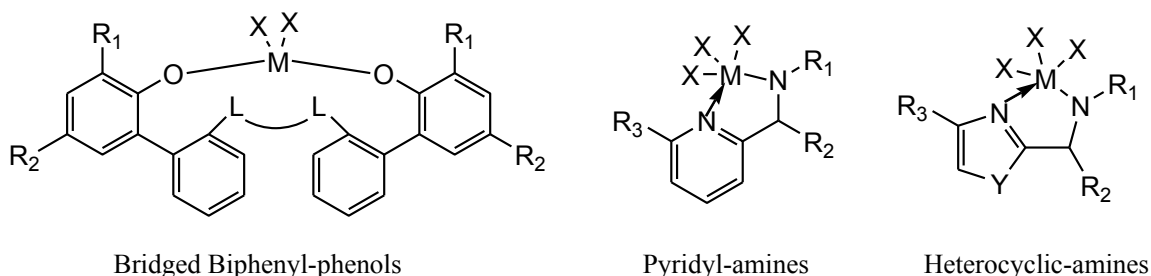


Figure 19. Schematic representation of the catalyst families studied in this work.

The initial screening of the catalyst candidates was carried out in both solution polymerisation and in slurry polymerisation by supporting selected complexes on silica support. The aim was to use HTS techniques to rapidly assess the capabilities of different catalyst families. The polymerization experiments were carried out with PPR (Parallel Pressure Reactor)^{40,147,148} and analysed with Rapid GPC¹⁷⁰ and DSC measurements. The most active catalysts were chosen to be studied further using broader conditions. These included amount of hydrogen, usage of comonomer like ethene, propene or other α -olefins and adjusting the polymerization temperature. By this way it was possible to control the activity of the catalyst and the Mw and crystallinity of the polymer product.

As expected the hydrogen content did not only have an effect on the Mw weigh but also to activity of the catalyst.¹⁷¹ The enhancement in the activity is most likely due to the fact the hydrogen is able to reactivate the dormant catalyst sites which are formed after 2,1-insertion of the monomer.¹⁷

The first screening experiments revealed that the heterocyclic amines were both the most active catalyst and also produced polymer with highest Mw (Figure 20). The DSC analysis of the selected polymer samples revealed that homo-polymers have melting points close to 240°C which is indicative for isotactic P4MP1.⁴⁹ On the basis of these results the heterocyclic-amine, namely thiazole and imidazole complexes bearing several different substituents including di-*iPr*-Ph, naphthyl, biphenyl, 2-methyl-benzothiophene, *o*-tolyl, phenyl, catalysts were chosen for further studies. The activation conditions were optimized for these selected catalysts by using both PMAO-IP, a MAO-type activator, and borate activators. The PMAO-IP activator proved to be more efficient and several experiments were carried out to optimize the Al:M ratio. The optimization study revealed that PMAO-IP activator with Al:M ratio of 400 gave the most active catalyst under used conditions. Thiazole amine-based catalyst was the one with the best overall performance and it was used under the optimised conditions in the polymerization of several homo- and copolymers of 4M1P.

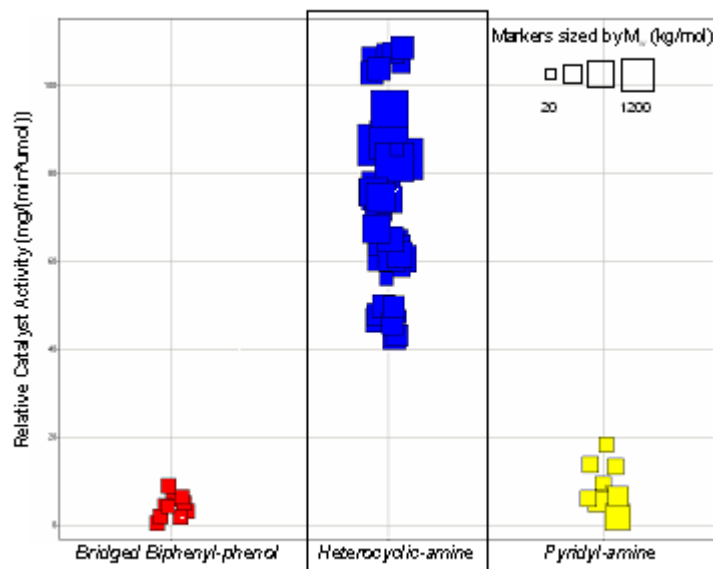


Figure 20. Results from the broad screening of the selected catalyst families. Heterocyclic amine catalyst families displayed the best overall performance in terms of activity and molecular weight capability.

The polymers obtained with the optimised catalyst were again analysed with Rapid GPC and DSC. The DSC results displayed in the Figure 21 clearly illustrate the known dependency between comonomer content and melting temperature of P4M1P.⁴⁹ Since the homo-polymers are clearly isotactic, the decrease in polymer melting point is evidently resulting of the incorporated comonomer, not from stereoerrors in the P4M1P chain. Also it can be seen that the chain length of comonomer has a clear effect on the melting temperature: monomers with longer alkyl chain induce rapid decrease in melting temperature of P4MP1. These results also demonstrate that the T_m can be easily controlled by techniques used in this work and by selecting appropriate comonomer.

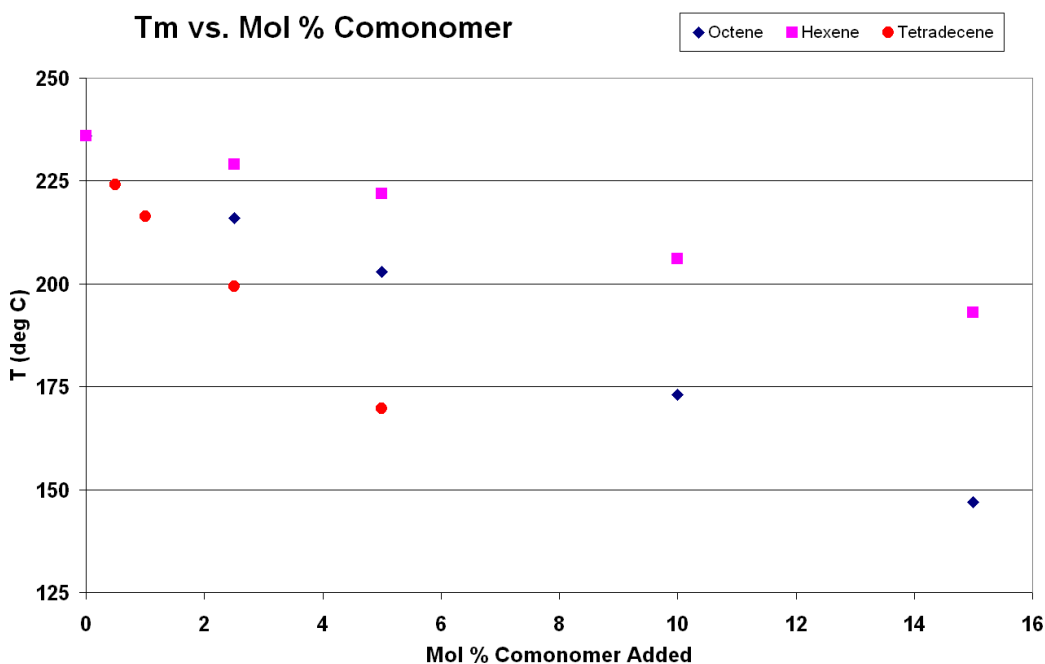


Figure 21. Effect of comonomer content and identity with melting temperature of P4MP1.

After analysing these polymers with Rapid GPC and DSC, selected samples were chosen to be studied in Rapid elongation at break and DMTA analysis. Figure 22 shows polymers' elongation at break as a function of modulus for the polymers synthesized using the thiazole amine catalyst. While it is clear that there is a trend, this becomes more apparent when only polymers with a certain molecular weight (1,000 kg/mol) are selected. These data show that the elongation at break for the copolymers is independent on the identity of used incorporating olefin (Figure 22).

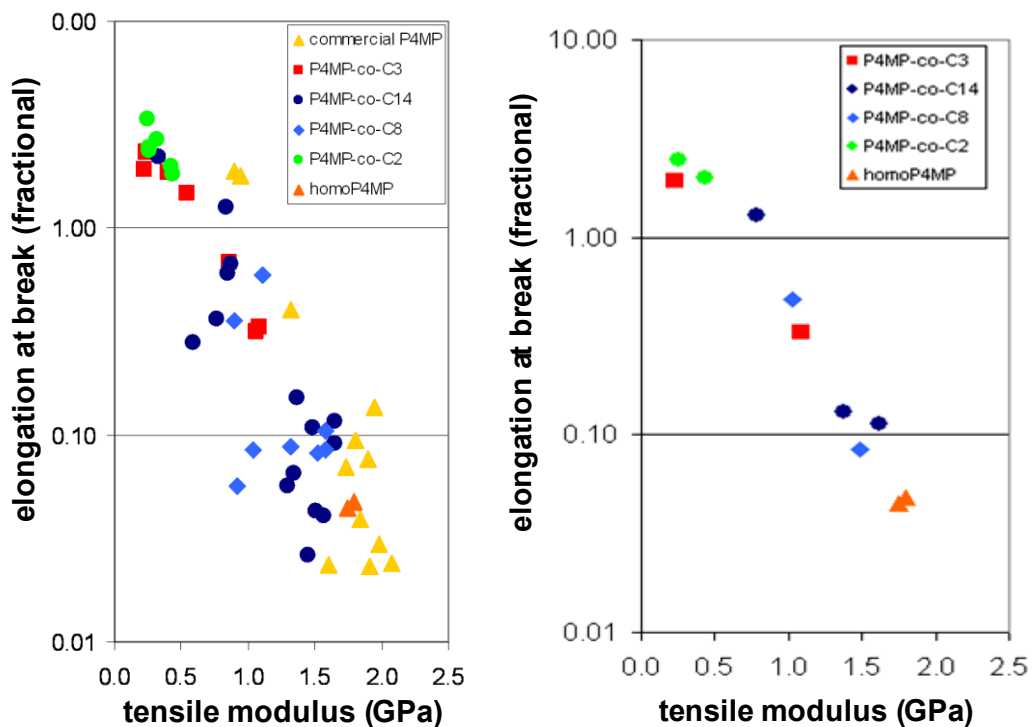


Figure 22. Elongation at break as a function of modulus for the P4MP polymers synthesized using the thiazole amine catalyst. On the right hand side are the results for polymers with similar molecular weight (1,000 kg/mol).

5 Conclusions

In this thesis new group IV metal complexes were synthesized bearing malonate- and pyrazolonate-based ligands. All the chosen ligand candidates were designed so that the electronic and steric surroundings of the metal center can be modified through relatively straightforward synthetic routes.

All the synthesized malonate based complexes exhibited low to moderate activities in ethene polymerizations regardless of polymerization conditions. Even though modifications on the ligand structure did not lead to notable differences in activity, an effect on the produced PE was observed: [O,O]-type malonate catalysts produced unimodal PE while [O,N]-type catalysts produced bi- or multimodal PE. It was also shown that in the case of [O,N] catalysts the polymerization conditions affect the ratios of high- and low Mw of the PE product.

A more pronounced effect of the ligand structure was observed among the pyrazolonato-catalyst family. The activities of the studied catalysts varied from low to high and also the PE product was affected by the choice of catalyst structure. By varying the catalysts structures, uni- or bimodal polymers with narrow or relatively broad polydispersity were obtained. The catalyst **9-Ti** was the only one to behave as a single-site catalyst, producing PE with a PDI values close to 2.

Furthermore in this thesis known Group IV metal complexes were studied in the polymerization of 4M1P. The selection of catalyst candidates were done on the basis of propene polymerization results. High through-put techniques were used to optimize the polymerization conditions and to produce a number of different type homo- and copolymers of P4M1P and to study their properties. This study exhibited the benefits of HTS techniques in the discovery of new polymerization catalysts. It is also the first example of using rapid mechanical testing techniques in combination with high throughput synthesis techniques. The combination of high throughput synthesis techniques with rapid mechanical testing techniques these techniques enabled the fast production and evaluation of a new family of polyolefins with desired physical properties.

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